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THE REVERSIBILITY OF SULPHIDE SOLS AND THE PROTECTIVE ACTION OF HYDROGEN SULPHIDE[1]

BY S. W. YOUNG AND WIN R. GODDARD

Introduction

It is generally considered that the insoluble sulphides of the metals represent non-reversible colloidal systems; that is, that when precipitated by electrolytes the removal of the electrolytes does not cause the redispersion of flocculated material. In view of the fact that Linder and Picton[2] repeatedly dispersed flocculated sulphides, after washing free from electrolyte, by means of hydrogen sulphide, this classification of them as irreversible seems unjustified. For the most part the rôle of hydrogen sulphide in colloidal sulphide sols has been ignored, and the following investigations were undertaken to gain some more definite knowledge concerning this. Since the investigation was finished (May, 1915) Jnanendranath Muktopadhyaya[3] has called attention to an interesting protective action of hydrogen sulphide on arsenic sulphide sols against their flocculation by electrolytes. That this investigator has not reached the whole truth will be shown by results in this paper, and those to be given in a later one.

Experimental Part I

The experimental work upon which this investigation rests divides itself into two parts: (1) Experiments demonstrating the complete reversibility of several colloidal sulphides with respect to hydrogen sulphide; (2) the protective effect of different concentrations of hydrogen sulphide on zinc sulphide in the presence and absence of electrolytes.

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[1] Abstract of a thesis presented to the Faculty of Stanford University by Win R. Goddard in partial fulfillment of the requirements for the degree of Master of Arts, May, 1915.

[2] Jour. Chem. Soc., 61, 114 (1891).

[3] Jour. Am. Chem. Soc., 37, 2024 (1915).

*(1) The Dispersion and Coagulation of Some Metallic Sulphides
by Repeated Addition and Removal of Hydrogen Sulphide*

    In order to have such experiments under the best possible
control with respect to the addition and removal of both
electrolytes and hydrogen sulphide, some type of dialyzing
apparatus seemed most likely to give satisfaction.   The ap-
paratus shown in Fig. 1 was devised and proved to be entirely
adequate and convenient for the purpose.   A is a glass
cylinder, 20 cm high and 5 cm in diameter.   Fitting tightly
into the mouth of this cylinder is a turned cork stopper through
which are three openings, two small and one large.   Through
the small openings are introduced, respectively, a glass tube
connecting with the burette C, and the glass stirrer F, which is
introduced through the oil seal G.   Through the large opening
is introduced the glass collar H which is of the same diameter
as ordinary dialyzing parchment tubing, a piece of which, E,
is tied to the lower end of the glass collar.   The lower end of
the parchment tube is gathered together and tied tight so as
to form a bag.   The upper end of the glass collar is closed
with a tightly fitting cork stopper, through holes in which are
introduced, (1) an escape tube for hydrogen sulphide, J, (2)
a tube, K, leading to a constant level device, D, and a tube, I,
leading from the lower end of B, from which a supply of dis-
tilled water, saturated with hydrogen sulphide or free from
it, may be drawn at will.   Water comes from a supply tank
above and trickles through the funnels in the tower.   Accord-
ing as one does or does not admit hydrogen sulphide through
the tube Y, the water which enters the dialyzing bag through
I is saturated with hydrogen sulphide or free from it.

    In order to operate the apparatus, the stirrer F is first
started.   A solution of a salt of the metal whose sulphide is
to be studied is placed in C.   A slow stream of water saturated
with hydrogen sulphide is allowed to pass into E, whence
some of the hydrogen sulphide diffuses into the water in the
outer cylinder.   While everything is running in this way the
solution of the salt from C is admitted, a few drops at a time,
at considerable intervals.   The sulphide is thus produced in the

cylinder and electrolytes formed are continually dialyzing
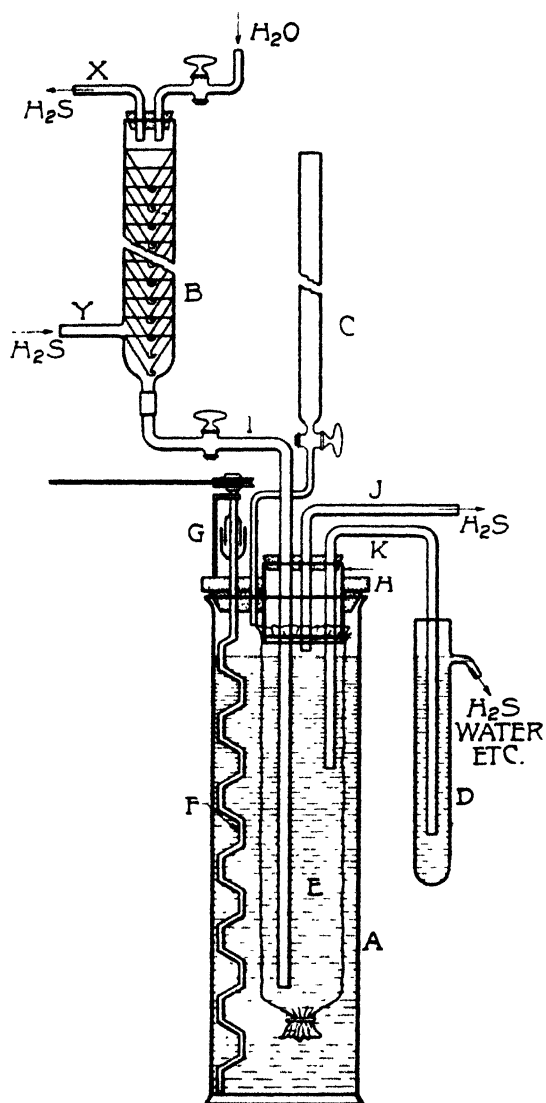
Fig. 1

inward into the bag E from which the stream of water carries them off through K.

It frequently happens that in introducing the solution of the salt, there is first formed a certain amount of flocculated sulphide. This, however, disperses sooner or later, under the influence of the stirring and the hydrogen sulphide. It was in general our practice to wait until the sulphide formed was to all appearances completely dispersed before adding another portion of the salt. A sulphide sol being once obtained in the foregoing manner, its conduct under the influence of the presence or absence of hydrogen sulphide could be alternately observed for any desired periods of time.

Cadmium Sulphide.—The first sol to be studied with the assistance of the apparatus was that of cadmium sulphide. As the procedure followed in this case was closely adhered to in all subsequent ones, a fairly circumstantial account of it will be given here once for all.

On September 21st everything was made in readiness and the apparatus started. After water saturated with hydrogen sulphide had been passed through for a time sufficient to replace the pure water originally in the cylinder and dialyzing bag with a strong solution of hydrogen sulphide, a few drops of cadmium acetate were run in. The sulphide formed dispersed freely and rapidly. From time to time additional acetate was run in until the sol formed was of a very deep yellow color, and seemingly quite opaque. Following this, the stream of hydrogen sulphide water was kept going for four hours or more, with continued stirring, during which time a very large amount of the acetic acid formed must have dialyzed out. At the end of the day the stirring and the water flow were shut off, while a slow stream of gaseous hydrogen sulphide was passed through the apparatus in order to maintain saturation and prevent access of air. In this condition the apparatus remained until the following noon. At this time there was no visible change in the conditions of the sol. There was only a very minute amount of flocculated sulphide which had settled to the bottom of the cylinder. A small sample of the sol was removed and placed in a tightly stoppered tube.

It remained for a long time seemingly stable but at the end of two months was wholly flocculated.

At noon on September 22nd, the stirrer was again started, and a stream of pure distilled water (without hydrogen sulphide) was passed through the apparatus. In this way the hydrogen sulphide in the sol would gradually dialyze out. After fifteen hours of this treatment there were perceptible signs of coagulation, and on stopping the stirrer for a few moments there was an easily noticeable settlement of flocculated sulphide. It was not, however, until after three days of continuous dialysis that flocculation was complete and the liquid remaining after settling showed no further traces of the yellow opalescence indicating dispersed sulphide.

On September 25th after the above condition had been reached, without otherwise interrupting the operation of the apparatus a current of hydrogen sulphide was started through the absorption tower B. The result of this was that the pure water in the dialyzing bag was replaced by saturated solution of hydrogen sulphide. Some of the hydrogen sulphide dialyzing out into the liquid in the outer cylinder would exert whatever influence it might have on the flocculated sulphide. Within a couple of hours the sulphide was seemingly completely redispersed. The flow of the gas was, however, continued for ten hours, after which the apparatus was allowed to stand for two days, perfectly quiescent save for the slow stream of hydrogen sulphide gas to maintain saturation and exclude air. After this time the sol was seemingly in a perfectly dispersed condition, showing no signs of settling.

These operations of coagulation and redispersion were repeatedly carried out and always with the same result. The only difference to be noticed was a tendency, upon repetition, for the period required for coagulation to become longer, and that for redispersion to become shorter. This effect might at first sight seem to be referable to the continual dialyzing out to greater and greater degree, of the last remnants of acetic acid formed in the reaction. But since acetic acid does not, even in high concentrations, flocculate most sulphide

sols, the explanation is not tenable.   It is, therefore, probably
referable to changes in the physical condition of the sulphide
itself, a matter which will be made subject of further study.

Zinc Sulphide.—An exactly similar study of zinc sul-
phide was made.   It conducted itself in all ways similarly to
cadmium sulphide except that it was more readily coagulated
and less readily dispersed.

Mercuric Sulphide.—The conduct of this substance was
in all ways similar to that of the above sulphides.   In readi-
ness of dispersion and difficulty of coagulation it seemed
closer to cadmium than to zinc.

Lead Sulphide.—This sulphide showed the same general
conduct as those above, although exhibiting some peculiarities.
On first forming, a very heavy black sol was produced.   This,
however, proved unstable, and in about half an hour had largely
flocculated even in the presence of the hydrogen sulphide.
This flocculation was not complete, however, but left a per-
manent brown sol of small concentration.   This sol followed
the same conduct as those of the sulphides of cadmium, zinc
and mercury.   It flocculated on removal of hydrogen sul-
phide and redispersed when hydrogen sulphide was again
introduced, and the flocculation became more difficult and the
dispersion more ready upon repetitions of the operations.
The difference in the conduct of the lead sulphide is, therefore,
due only to the relatively small amount of it which can be
dispersed in a given volume of water.

Arsenic Sulphide.—A similar study of arsenic sulphide
(using a solution of the trioxide) was also made.   The sol
obtained in this case did not flocculate in the apparatus after
many days of dialysis.   However, samples of the sol saturated
with hydrogen sulphide and those from which the hydrogen
sulphide had been dialyzed out, were taken and preserved in
sealed tubes.   At the end of two months those from which the
hydrogen sulphide had been removed had flocculated in every
case, while those containing hydrogen sulphide had in no
case flocculated after six months.   Thus the divergent con-
duct of arsenic sulphide is to be ascribed merely to the un-

usual length of time required for the unstable, hydrogen sulphide-free sol to flocculate. In a subsequent paper a similar and even more exaggerated conduct on the part of copper sulphide will be shown, sols of this material when dialyzed free from hydrogen sulphide requiring six or more months for flocculation.

In summarizing the results of this first part of the investigation, it seems quite clear that the sulphide sols are readily reversible with respect to hydrogen sulphide. Since the removal of hydrogen sulphide from sols by bubbling through of hydrogen does not in general produce instability of the sol, it must be concluded that the removal by that means is, in a reasonable time of treatment at any rate, very incomplete, as compared with the removal by dialysis. The results of our experiments seem to make it reasonable to assume that the dispersed substance in these sulphide sols is a dissociable compound of the sulphide with hydrogen sulphide, while the flocculated sulphides are either free from hydrogen sulphide or contain relatively little of it. That flocculated sulphides formed in the presence of electrolytes contain some excess hydrogen sulphide is, of course, known from the work of Linder and Picton. It is now clear that the condition of a sulphide in contact with water is determined not only by the amount and character of the electrolyte, but is enormously influenced by hydrogen sulphide. Colloidal sulphides are irreversible only from failure to truly reverse the conditions, of primary importance among these being the resupplying of hydrogen sulphide, and a good allowance of time.

Experimental Part II

The following experiments were undertaken to determine, if possible, the influence of the concentration of the hydrogen sulphide on zinc sulphide. An apparatus was devised by means of which tubes containing the sulphide and water could be saturated with hydrogen sulphide at pressures varying from minimal ones to several atmospheres. The design of the apparatus is given in Fig. 2. It consists of a container,

G, for liquid hydrogen sulphide, kept in a bath of liquid air and ether. After this had been filled from one-half to two-thirds full with the liquefied gas (taken from an ordinary Kipp generator) the opening at I was closed by a glass plug and Khotinsky cement. The tube containing the material which was to be subjected to the influence of the hydrogen sulphide is shown at K. The flexible coils of the apparatus
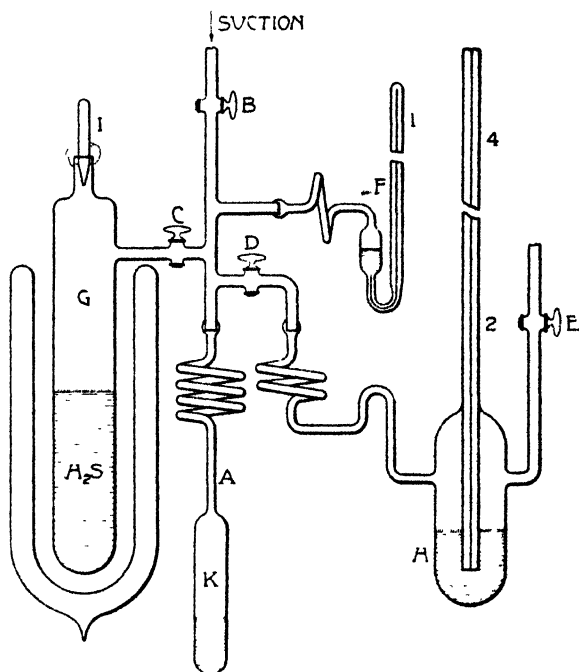
Fig. 2

are all of small lead or copper tubing. The rest of the apparatus is of glass. H is an ordinary barometer-manometer for pressures less than one atmosphere. F is an air-filled manometer for pressures greater than one atmosphere. The tube K having been attached to the apparatus at A, the next step was to replace all air in the apparatus. This was accomplished by closing the cocks at D, and C, and evacuating the apparatus through the cock B, after which B was closed and C opened. The cooling bath was then lowered

away from G and hydrogen sulphide allowed to gasify into the apparatus until the manometer F showed one atmosphere pressure. The cooling bath was then replaced and cock C closed. This whole operation was repeated several times until it was certain that the whole apparatus, except that between D and E, was free from air. Air was removed from this portion by opening C, lowering the cooling bath until F showed somewhat more than one atmosphere, then opening D and E and allowing a considerable volume of gasified hydrogen sulphide to flow out at E.

All this being accomplished, the pressure in the apparatus was adjusted to that desired, reduction of pressure being obtained by suction and increase of pressure by warming G and admitting gas through C. The contents of the tube K were repeatedly shaken to ensure saturation, and the pressure readjusted, until upon further shaking of K it remained constant at the desired value for fifteen or twenty minutes, after which the tube was sealed while still under the given pressure, by a method which will now be described. Fig. 3 shows the form of tube used. On account of the difficulty of filling through the constriction in the tip, the bulb and a short neck (below *a*) was made separately from the tip which is shown at *b*. After the material to be treated had been placed in the bulb, the tip was sealed on and a small lump of paraffin (*c*) dropped into the tip where it lodged just above the constriction. In this condition the tube was attached to the charging apparatus and when once saturated with hydrogen sulphide at the desired pressure, it was very gently warmed just above the constriction. This melted the paraffin which flowed down and congealed in the constriction, thus making a temporary seal. The tube was then removed from the apparatus and the tip drawn off and permanently sealed, as at *d*.
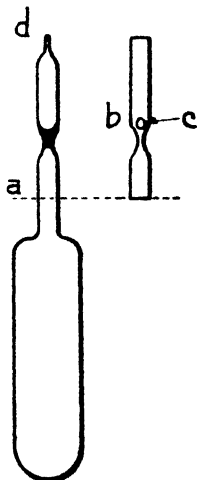
Fig. 3

With the assistance of this apparatus several sets of tubes, as hereafter described, were prepared and kept under observation for several months. The first set was prepared by placing in each 5 cc of $N/10$ $Zn(C_2H_3O_2)_2$ solution, and the tubes, after thorough precipitation and saturation with hydrogen sulphide, were sealed off at the following pressures of hydrogen sulphide: 0.5, 0.75, 1, 1.25, 1.5, 1.75, 2, 3, 4 atmospheres. The phenomena on charging these tubes were very interesting. In all cases the first admission of the hydrogen sulphide produced a very white milky liquid. On standing and acquiring equilibrium with the various pressures of hydrogen sulphide, the conduct of the tubes was different according to the pressure of the gas. The tube at 0.5 atmosphere changed but little, while with those at higher pressures there was an increasing clearing of the liquid, so that those at 2, 3 and 4 atmospheres were nearly water-white, with no precipitate, and showed only a faint bluish opalescence. The tubes were in this condition when they were sealed off and set aside.

This highly dispersed condition was not stable, for in all cases the strong milkiness returned and there were signs of settlement on standing. The tubes at lower pressures reacted in this way more rapidly than those at high pressures, but so far as could be judged, none the less completely. After a couple of days there was no further visually discernible change in any of the tubes, and so far as could be determined, there was a maximum degree of dispersion at about 1.5 atmospheres, there being greater tendency to settlement in tubes at higher as well as at lower pressures. There was, however, this difference to be noted, that at low pressures, notably at 0.5 atmosphere, the settled material had more the character of a flocculate, while at higher pressures it seemed to show no flocking whatever, but to be of the nature of a smooth cream.

The tubes were kept under observation for four months. At the end of this time the tube at 0.5 atmosphere seemed practically completely settled, the liquid above it being very transparent and showing only a slight trace of opalescence.

With tubes at higher pressures the opalescence of the liquid increased regularly with the pressure up to 1.5 atmospheres, while the amount of settlement showed a corresponding decrease. From 1.5 atmospheres up, the tubes were so nearly alike that they were difficult to distinguish from one another.

The results obtained with this set of tubes show that at the time of its formation, zinc sulphide is susceptible of a very high degree of dispersion by hydrogen sulphide; that these highly dispersed sols are unstable, and that the particles contained in them gradually increase in size and become capable of settlement; that, after standing for four months, there is abundant evidence of the protective action of hydrogen sulphide, this protective action attaining its maximum at about 1.5 atmospheres.

In the second set of tubes, an effort was made to gain an idea of the effect of various pressures of hydrogen sulphide on zinc sulphide in presence of varying amounts of potassium chloride. The hydrogen sulphide pressures chosen were 1, 2, 3, and 4 atmospheres, and for each of these pressures three tubes were prepared, containing solutions, respectively, N, 10, N, 100 and N, 1000 KCl in addition to being N 10 with zinc acetate. The twelve tubes, after being charged with hydrogen sulphide to the desired pressures and sealed off, were allowed to stand for four months and observations of the condition made. They were then rotated for two days and allowed to stand for another month in order to determine if such treatment produced any permanent change in their condition. None was found.

In so far as the influence of hydrogen sulphide was concerned, the condition of these tubes agreed with those of the first set. The dispersion increased to two atmospheres, and seemed to show a slight decrease from two atmospheres up. This may perhaps be explained as caused by two effects of the hydrogen sulphide—a specific dispersing effect and its effect as an electrolyte.

As concerns the effect of the potassium chloride, the tubes which were $N/1000$ with this reagent showed complete

flocculation in no case, while in all cases those that were $N/10$ showed it.   At 1 atmosphere of hydrogen sulphide the $N/100$ tubes were completely flocculated, while in the corresponding tubes at higher pressures of hydrogen sulphide there was complete flocculation in no case.   There is in this fact, of course, evidence of protection by hydrogen sulphide against electrolytes, a protection which increases with the concentration of the hydrogen sulphide.

Special Experiments

A number of extra tubes for hand experiments were prepared in the course of the work.   If such tubes, after having stood in a well-defined state of dispersion for four or more months, were broken at the tip and the hydrogen sulphide allowed to escape, complete flocculation occurred within a few hours.

Two identical tubes, charged to two atmospheres with hydrogen sulphide, were allowed to stand for two months, in order that virtually complete equilibrium might be attained. At the end of this time one of the two tubes was placed in boiling water for a few minutes, while nothing whatever was done with the other tube.   The result of the boiling was to make the contents of the tube very milky and considerable flocculation was noticeable.   It was then taken from the hot bath, and allowed to stand quietly by the side of the check tube.   It gradually cleared and at the end of two months was not visually distinguishable from the other.   This seems to indicate that there is also a thermal reversibility of colloidal zinc sulphide in contact with hydrogen sulphide, for, although the effect might be partly explained as due to driving the hydrogen sulphide from the liquid to the gas phase by heating, it is scarcely probable that by this means the hydrogen sulphide concentration in the liquid phase could be reduced to so low a minimum as would be necessary for the appearance of so much flocculation.   After the heating, the tube corresponded with the appearance of tubes under less than 0.5 atmosphere of hydrogen sulphide.

Summary

A new apparatus and method for the preparation and purification of the sulphide sols is described.

Evidence is brought forward to show the complete reversibility of several such sols with respect to hydrogen sulphide.

The dispersive effect of hydrogen sulphide on zinc sulphide increases up to 1.5 or 2 atmospheres, and possibly decreases somewhat at higher pressures.

Evidence of the protective effect of hydrogen sulphide against the flocculation of zinc sulphide by potassium chloride is given.

An experiment is cited which makes it seem probable that there is a thermal reversibility of zinc sulphide sols in contact with hydrogen sulphide.

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COLLOIDAL SOLUTIONS OF COPPER SULPHIDE[1]

BY S. W. YOUNG AND ROLAND NEAL

With the discovery that certain natural copper sulphides yield colloidal copper sulphide on treatment with hydrogen sulphide,[2] and the probability that colloidal solutions of copper sulphide may play a not unimportant part in the processes involved in the secondary enrichment of copper sulphide ore beds, a knowledge of the properties of such solutions from the chemical point of view becomes a matter of considerable interest. In the following paper are given the results of a preliminary investigation of such solutions, and while the researches are by no means to be considered as complete, considerable material of interest is already in hand and given here.

The composition of the sulphide content of a colloidal solution of copper sulphide is at the present time a very uncertain matter. Older investigators maintain that by the action of hydrogen sulphide on cupric compounds in the presence of water, a mixture of cupric and cuprous sulphides is formed, while Posnjak, Allen and Merwin[3] claim that only cupric sulphide is thus formed. On the other hand, it has been observed in this laboratory that sulphide precipitated from cupric sulphate by hydrogen sulphide with exclusion of air and sealed up in an atmosphere of hydrogen sulphide shows the presence of distinct crystals of sulphur after some months' standing. There seems to be at least some uncertainty as to the nature of the sulphide in the solutions used in this work, all of which were prepared from cupric compounds.

The scope of the present investigations cover: (a) the preparation of colloidal copper sulphide solutions (copper

[1] Abstract of a thesis presented by Roland Neal to the Faculty of Stanford University in May, 1915, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] Clark: Bull. University of New Mexico, 1914, Chem. Series, Vol. 1, No. 2.

[3] Jour. Econ. Geol. 10, 528 (1915).

sulphide sols); (*b*) influence of electrolytes on the dispersion of amorphous copper sulphide; (*c*) flocculation by electrolytes; (*d*) influence of hydrogen sulphide on the flocculation by electrolytes; (*e*) migration velocity in the electric field; (*f*) influence of electrolytes and of hydrogen sulphide on the migration velocity.

Experimental

Methods of Preparation of Copper Sulphide Sols.—For the most part the methods of preparation used in this work are those which have already been used, and are in the main described in Svedberg's "Herstellung kolloider Lösungen anorganischer Stoffe." Solutions were prepared in a variety of ways in order that it might be determined what influence the mode of preparation had on the properties of the product. Colloidal solutions were therefore prepared by the following three methods:

1. Agitation of well-washed copper hydroxide with hydrogen sulphide water.

2. Agitation of well-washed copper carbonate with hydrogen sulphide water.

3. Agitation of well-washed freshly precipitated copper sulphide with hydrogen sulphide.

In all cases the solution was freshly saturated with hydrogen sulphide from time to time and the containers were kept carefully stoppered to exclude air. They were also kept out of direct light which accelerates the oxidizing action of any air that may gain admission. The following sols were prepared as specified and in the latter part of this work will be referred to by the numbers given them here.

Sol 1.—Two grams of copper sulphate were dissolved in 300 cc of distilled water, and the solution brought to faint permanent alkalinity with sodium hydroxide. The precipitated hydroxide was filtered off and thoroughly washed with distilled water. It was then placed in a large volume of freshly distilled water and allowed to stand for ten months, after which the water was decanted off and 800 cc of fresh water added. On now passing hydrogen sulphide into the

liquid, the conversion of the hydroxide into finely dispersed sulphide began almost immediately. For a period of ten days, hydrogen sulphide was passed through the solution at frequent intervals, and the solution was subjected to gentle agitation for a period of an hour after each charging with hydrogen sulphide. This sol proved to be perfectly stable. After standing for two and one-half months there was no evidence of any tendency to settle. The color was very dark even when the solution was diluted 1 to 5 with water.

Sol 2.—This was prepared similarly to the above, except that the copper was precipitated as carbonate (by sodium carbonate) instead of as hydroxide. The carbonate was, however, washed less thoroughly than the hydroxide, the whole preparation in this case being completed within two weeks. In general appearance the sol was similar to Sol 1. Kept saturated with hydrogen sulphide and stoppered, it showed no deterioration and no settlement after many months.

Another preparation, identical with Sol 2, but in which the copper carbonate was washed by repeated boiling with water, was not so successful, the dispersion with hydrogen sulphide being both less rapid and less complete. This sol was not used in any of the work to be described.

Sol 3.—This was made by dissolving copper sulphate in water (amounts used as above), precipitating by means of hydrogen sulphide, repeated washing by decantation for a month, and finally dispersing by repeated treatment with hydrogen sulphide accompanied by agitation. This sol maintained itself in good condition, showing no settling after one year.

Sol 4.—This was prepared in the same way as Sol 3, except that the copper sulphate was strongly acidified with sulphuric acid before the precipitation of the sulphide. Upon attempting to disperse the sulphide thus formed after washing as for Sol 3, the result was unsatisfactory, the dispersion not forming at all readily. The precipitate was therefore dialyzed for two weeks, after which it yielded to dispersion with the same ease as that used in preparing Sol 3.

Sol 4 (a).— This was in all respects a duplicate of Sol 4.

Sol 5.—This was prepared by adding sufficient ammonia to the copper sulphate solution to redissolve all copper hydroxide, before precipitation with hydrogen sulphide. Otherwise the preparation was identical with Sol 4.

Effect of Electrolytes on the Rate and Degree of Dispersion of Copper Sulphide by Hydrogen Sulphide.—While the flocculation of colloidal solutions by electrolytes has been extensively studied, little is known of the influence of electrolytes in inhibiting dispersion. Considerable time was devoted to an attempt to get some light on this point, but it was soon evident that the experiments would demand an elaborateness of technique and apparatus that would make an extensive investigation in this direction impracticable in the time at disposal. Before abandoning this work, which it is the intention to take up later in more thorough manner, some results sufficiently interesting to be recorded here were obtained.

The method employed was to place in each of several testtubes the same small amount of copper sulphide (actually the carbonate, thoroughly washed, was used). To the first were then added 5 cc of pure water, to each of the others were added 5 cc of the electrolytes to be studied each at its desired concentration, this being, of course, always smaller than that necessary to produce flocculation. Hydrogen sulphide was then bubbled slowly through and the dispersion determined by observation from time to time. In all cases where dispersion took place it seemed to be complete after twenty-four hours. The results were, in general, that in like concentrations the inhibitions to dispersion were in the same order as the flocculating powers of the electrolytes, as is, of course, to be expected. One marked peculiarity was however found in the unexpected action of the alkaline hydroxides. These are usually held to stabilize the sulphide sols up to a certain point, but in our work they seemed to show the same inhibition of dispersion as the equivalent solutions of alkaline chlorides. Curiously enough, however, they did show a marked initial

acceleration in the rate of dispersion, and probably a marked initial increase in the degree.

If three tubes were taken, as above, all containing a small amount of copper carbonate, one containing also pure water, the other two containing $N/1000$ KCl and $N/1000$ KOH, respectively, and hydrogen sulphide bubbled through all three simultaneously, the one containing the potassium hydroxide would show a far more rapid and extensive dispersion than the others, while after a few hours this would have reflocculated to a great extent and the condition of the tube after 24 hours would be about the same as that of the one containing potassium chloride. In the mean time, the dispersion in the tube without electrolyte will have far outdistanced the other two.

While there seems to be, at present, no satisfactory explanation of this phenomenon, it is believed that there may be found in this sort of experiments the nucleus for an interesting method of studying the reverse reaction to flocculation.

Effect of Removal of Hydrogen Sulphide from Copper Sulphide Sols.—Some experiments were carried out to determine to what extent the stability of a copper sulphide sol is dependent on the continued presence of hydrogen sulphide. In this work the apparatus described by Young and Goddard[1] was used. In the parchment bag was placed a one-thousandth normal solution of copper acetate and hydrogen sulphide was bubbled continuously through the surrounding dialyzing water. It slowly diffused into the acetate solution forming the sulphide, while the acetic acid formed gradually dialyzed outward. While there was at first some flocculated sulphide formed, this gradually dispersed under the influence of the stirring and of the hydrogen sulphide, until after two days of treatment at intervals, the sol showed no tendency to settle. When this condition had been reached, the hydrogen sulphide water in the outer compartment was replaced by pure water, and this replacement was repeated every day for ten days, thus ensuring a practically complete removal of free hydrogen

[1] Jour. Phys. Chem., 20, 3 (1916).

sulphide from the sol. There was no sign of settlement at the end of the ten days, nor was there after an additional twelve days of standing. After this, the apparatus was opened and a sample removed, which was placed in a tightly stoppered bottle. There was no odor of hydrogen sulphide. After standing for five months this sample showed considerable flocculation and settlement, which in no case happened with sols kept saturated with hydrogen sulphide, even after a period of a year.

To the sol remaining in the dialyzing bag there was added a fresh amount of copper acetate solution, sufficient to make the whole about three thousandths normal. This was subjected to the same treatment as the first solution. After complete dispersion had taken place, and the hydrogen sulphide had been completely dialyzed out, the sol was bottled and stoppered and set away for observation. After two months it was seemingly unchanged, but after four months it was almost wholly flocculated. It is thus quite certain that copper sulphide sols depend for their stability upon the presence of hydrogen sulphide, which agrees with the results of Young and Goddard[1] on the other sulphides. They may, however, maintain themselves in the form of the unstable dispersion for long periods of time.

Flocculation by Electrolytes. — The literature concerning the flocculation of sulphide sols is so extensive and so well known that it need not be recited here. As particularly concerns copper sulphide sols, Spring and du Boeck[2] carried out flocculation tests on this substance, the method being to add 10 drops of the sol to 10 cc of solutions of various concentrations of the electrolytes to be investigated. In the stronger electrolyte solutions distinct flocculation or turbidity appears, in the weaker ones it does not, a tube to which 10 drops of the sol had been added to 10 cc of pure water being used as a comparison tube. The electrolytes arranged themselves in the

[1] Loc. cit.
[2] Bull. Soc. roy. belg. (2) 47, 165 (1887).

same general order of flocculating power as was found later by Freundlich[1] in his study of arsenic sulphide sols, and as had been found previously by Schultze[2] for antimony sulphide sols even though the experimental methods employed by the different investigators varied considerably.

Flocculation experiments were carried out in this work, chiefly to determine whether or not the sols from different sources conducted themselves materially differently from one another. The method used was to prepare a solution of a given electrolyte of a concentration double that which was desired in the final solution. This was saturated with hydrogen sulphide, after which 2 cc of it were mixed with 2 cc of the sol to be investigated. After mixing, hydrogen sulphide was again passed through the mixture for a few moments, after which the tube was tightly stoppered and set away for observation. The period of standing which was chosen was twenty-four hours. If at the end of that time the liquid was still colored and turbid, it was considered to be not completely flocculated. In all cases in the following results, flocculation means that the settlement was complete, the liquid water-white and not opalescent. The period of twenty-four hours was chosen instead of a shorter one (Freundlich allowed one-half hour) because a set of preliminary tests showed that the results were more consistent after the longer period. The presence of hydrogen sulphide in the solution and an atmosphere of hydrogen sulphide above it, were found to greatly increase the regularity of the results obtained. Potassium, calcium and aluminum chlorides were investigated with regard to their flocculating effects. Sols 1 and 2 (see *ante*) were used, two sets of experiments being made with Sol 2, and Sol 1 being investigated at full concentration and in dilutions of 1–5, 1–10, 1–15 and 1–20, the dilution being in all cases made with water saturated with hydrogen sulphide. The results are shown in Table I. (+) indicates complete flocculation and (—) indicates incomplete flocculation.

[1] Zeit. phys. Chem., **44**, 129 (1903).
[2] Jour. prakt. Chem., (2) **25**, 431 (1882).

TABLE I

Concentrations of Electrolytes Necessary to Completely Flocculate
Copper Sulphide Sols

Sol	KCl		CaCl$_2$		AlCl$_3$	
	(+)	(−)	(+)	(−)	(+)	(−)
2	$\dfrac{3N}{100}$	$\dfrac{2N}{100}$	$\dfrac{8N}{10\,000}$	$\dfrac{7N}{10\,000}$	$\dfrac{3N}{100\,000}$	$\dfrac{2N}{100\,000}$
2	$\dfrac{4N}{100}$	$\dfrac{3N}{100}$	$\dfrac{10N}{10\,000}$	$\dfrac{9N}{10\,000}$	$\dfrac{3N}{100\,000}$	$\dfrac{2N}{100\,000}$
1	$\dfrac{3N}{100}$	$\dfrac{2N}{100}$	$\dfrac{10N}{10\,000}$	$\dfrac{9N}{10\,000}$	$\dfrac{5N}{100\,000}$	$\dfrac{4N}{100\,000}$
Dil. 1-5	—	—	$\dfrac{9N}{10\,000}$	$\dfrac{8N}{10\,000}$	—	—
Dil. 1-10	—	—	$\dfrac{9N}{10\,000}$	$\dfrac{8N}{10\,000}$	—	—
Dil. 1-15	—	—	$\dfrac{9N}{10\,000}$	$\dfrac{8N}{10\,000}$	—	—
Dil. 1-20	—	—	$\dfrac{9N}{10\,000}$	$\dfrac{8N}{10\,000}$	—	—

When compared with the results of Spring and du Boeck[1] the results show good agreement so far as potassium chloride is concerned. The results for calcium chloride are about 25 percent lower than theirs for barium chloride (they give none for the calcium salt) while the results for aluminum chloride are 50 percent or more lower than theirs for aluminum sulphate. Since the anion has but little influence on the flocculating power of an electrolyte for sulphide sols, it might reasonably be expected that the results for aluminum chloride and sulphate should show closer agreement. The discrepancy is, however, probably to be explained by the longer time given for reaching equilibrium in this work, as well as by the rather fundamentally different manner in which the experiments were carried out.

The results of the flocculation experiments show that the amount of electrolyte required does not vary appreciably with

[1] Loc. cit.

the source and manner of preparation of the sol, and that the amount of electrolyte required is independent of the dilution of the sol within wide limits.   This latter was found to be true within rather close limits by Freundlich[1] for arsenic sulphide sols.   '

Flocculation tests were also made upon sols from which the hydrogen sulphide had been removed by dialysis.   The results were the same as those obtained when the sols were saturated with hydrogen sulphide, for which reason it is not considered necessary to give numerical data concerning them.

From the results obtained in this work the relative flocculating powers of potassium, calcium, and aluminum for copper sulphide sols are:

$$1:39:875$$

Rate of Migration in the Electric Field.—The rate of migration of the copper sulphide in the sols under the influence of the electric field was studied quite extensively in order to determine the following factors:

(*a*) Reproducibility of results in successive experiments using the same sol under the same conditions.

(*b*) The influence of the origin of the sol on its rate of migration.

(*c*) The influence of dilution.

(*d*) The influence of electrolytes.

(*e*) The influence of hydrogen sulphide.

(*f*) The combined influence of hydrogen sulphide and electrolytes.

(*g*) The influence of oxygen.

The apparatus used in these experiments is shown in Fig. 1 and is practically self-explanatory.   Small platinum wires were used as electrodes and these were allowed to dip about 2–3 mm below the surface.   Readings were not begun until a well-defined flat migration surface had established itself.   In order to avoid the effect of light, the measurements were made in a darkened chamber.   The voltage employed

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[1] Loc cit.

was as near as possible to 100. With the equipment at hand, it was not always possible to maintain this with exactness, and many of the results are calculated to this voltage on the assumption that the migration rate is proportional to the potential fall. It has been the experience in this laboratory that attempts to have the electrodes bathed in pure water containing none of the colloidal material lead to more fluctuating results than are obtained when such device is not used, especially when the sols contain electrolytes or other easily diffusible materials. This is probably due to the fact that the conductor is no longer homogeneous as well as to the fact that electrolytes diffuse out into the pure water and materially alter the conditions at the surface of migration. While dipping the electrodes directly in the sol means increased electrolysis, it is nevertheless true that, judging from reproducibility and consistency of results, it is the lesser evil which is encountered in this way. All the results given below were obtained with electrodes dipping directly in the sol.

(a) *The Reproducibility of Results.*— For the purpose of determining the reproducibility of measurements on one and the same sol in different determinations, a portion of Sol 4 was diluted with $2^1/_2$ vols. of hydrogen sulphide water, and the whole

Fig. 1

thoroughly saturated with hydrogen sulphide. Five independent determinations of the migration rate were made on the same day and under identical conditions. Others were made at various intervals of time, often months apart. The results showed that the data obtained on the same day were in very close agreement, but that the rate of migration of the same sol might change quite materially with time. In the following, therefore, all measurements intended for com-

parison were made on the same day, as far as possible. In considering the whole set of results to be given, it is necessary to bear in mind that results obtained with the same sol at widely separated times, are not in general strictly comparable.
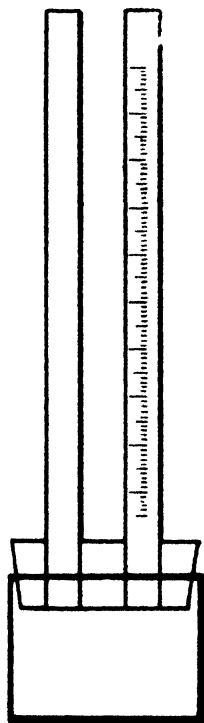
(*b*) *Influence of the Origin of the Sol on the Migration Rate.*—A considerable number of comparisons of migration rates of sols of different origin were made, with the result that in general the rates found were in no case in agreement, the magnitude of the disagreement often being very great. For illustration there are shown in Chart I the values obtained for
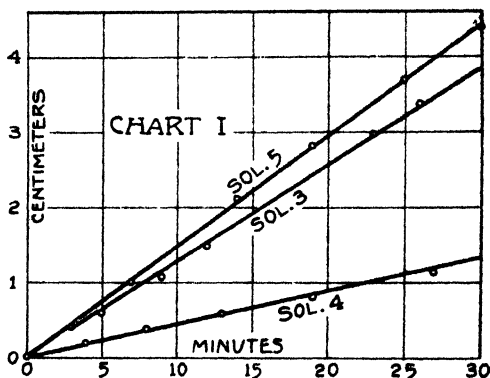
Sols 3, 4 and 5. It will be recalled that Sol 4 was made by dispersing copper sulphide precipitated from acid copper sulphate solution, while Sol 5 was made by dispersing copper sulphide precipitated from an ammonia solution of copper sulphate. Sol 3 was similarly prepared from neutral copper sulphate solution. The ordinates represent distances traveled in centimeters and the abscissae represent times. As will be seen, Sol 5 migrates about three times as rapidly as Sol 4.

This phase of the work was not carried further, the present purpose being rather to determine what factors could cause variations in the conduct of the sols, than to make a detailed study of them. It is the intention to extend this work in the near future.

(*c*) *The Influence of Dilution.*—A number of measurements of the rate of migration of a sol in its full concentration

and when diluted were made. In order to alter the condition of the sol as little as possible the dilution was always carried out with water saturated with hydrogen sulphide, and the gas bubbled through the diluted sol immediately after dilution, to ensure complete saturation.

It was found that the effect of dilution was invariably to increase the rate of migration. The results of two such sets of measurements are shown in Chart II. Here, as
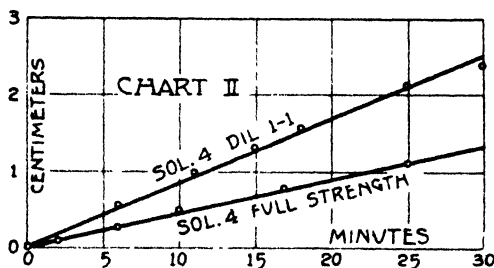
throughout the rest of this paper, it is not considered necessary to print the figures for the actual measurements obtained, for the actual values may be read off from the graphs with sufficient accuracy. The data in this case are for Sol 4 in full strength and diluted 1 to 1. The migration rate of the diluted sol is nearly double that of the undiluted.

(d) *The Influence of Electrolytes.* --The influence of electrolytes upon the migration rate of copper sulphide sols was subjected to a rather extensive study. Potassium and calcium chlorides were investigated at less than their flocculating concentrations, and a considerable number of concentrations of each was investigated. In this way there were obtained results from which the relative effects of the two electrolytes in equivalent concentrations could be obtained. All of the different sols were investigated and the influencing factor seemed to be fairly independent of the original migration rate of the sol. That is, whatever the initial value for the migration of the sol, this seemed to be multiplied to about the same extent by the same addition of electrolyte. Variations of the rates for the different sols with time and other causes

have made it impossible up to the present to obtain a wholly consistent set of results. For the most part the results on a given chart were obtained in a very short period of time, after a laborious series of preliminary measurements had made evident the danger of comparing results obtained at very considerable intervals of time.

A sufficient number of data to indicate clearly the main results obtained have been compiled and are shown in the following charts: Chart III shows the effect of successive additions of potassium chloride to Sol 4. The effect is to increase the migration rate. Chart IV shows the effect of
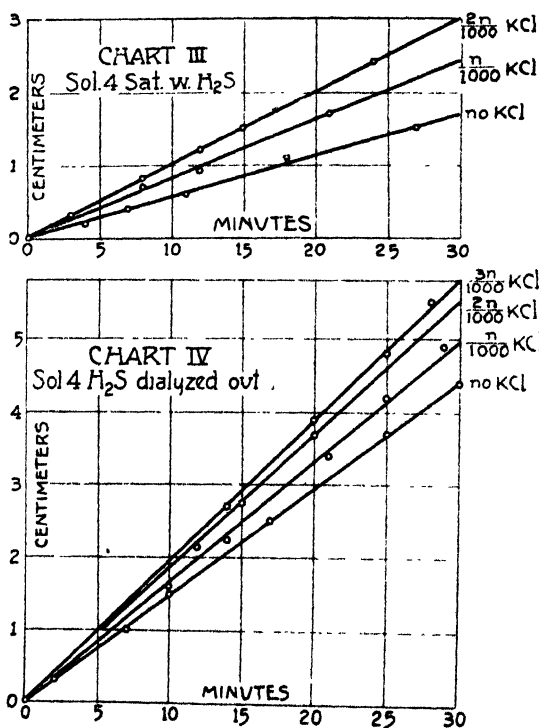
potassium chloride on the same sol after it had been previously dialyzed for a long period so as to remove all hydrogen sulphide. It will be noticed that the migration rate of the sol itself as well as mixtures of it with potassium chloride solu-

tions are all higher than the rates for corresponding solutions saturated with hydrogen sulphide, a matter to which reference will be made later. The effect of the potassium chloride is, however, the same in both cases, namely, to increase the migration rate. Chart V shows the effect of successive additions of potassium chloride to Sol 5, a sol of a high migration rate. The chart shows that the increase in migration rate is approximately proportional to the amount of potassium chloride added. Comparing Chart V with Chart III it is seen that
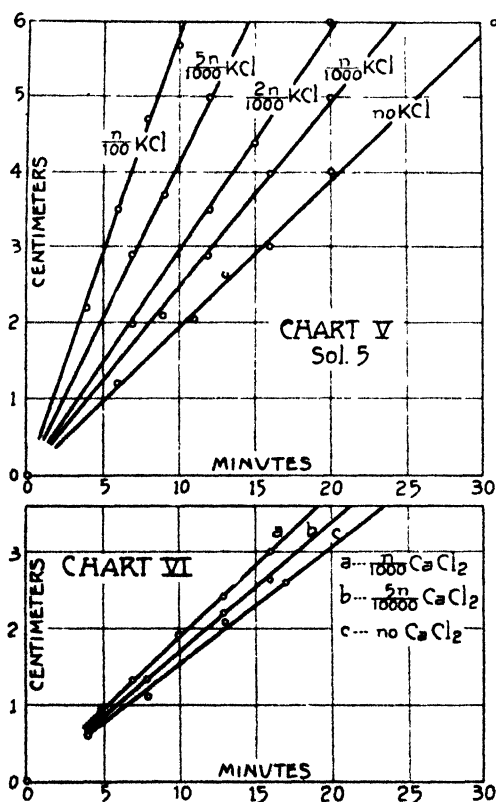
the increase of migration rate produced in the two cases by the same addition of potassium chloride is quite closely proportional to the original migration rate of the pure sol. Thus at the end of fifteen minutes, the distance migrated by Sol 4

is 1 cm, that by Sol 5 is 3 cm and the ratio $^1/_3 = 0.333+$. For the distances migrated at the end of the same period by the same sols to which potassium chloride has been added in $\frac{2}{1000}$ normality, we have, respectively, 1.5 cm and 4.5 cm, and the ratio $= 0.333+$. This is a fortunately chosen case, but in general the rule seems to hold fairly closely. The influence of the potassium chloride on the sol from which hydrogen sulphide had been removed is seen to be much smaller.

The effect of calcium chloride is shown in Chart VI. It is entirely similar to potassium chloride in its conduct. One thousandth normal is about the concentration of calcium chloride that will flocculate the sol in twenty-four hours; in fact, it is a trifle above it. It was nevertheless possible to carry out the migration measurements at this concentration, although flocculation occasionally occurred during the experiment.

Chart VII shows the relative influence on Sol 5 of potas-

sium and calcium chlorides at one-thousandth normal concentrations, the graph for the pure sol being added for comparison. As will be seen, the effect of the potassium chloride somewhat exceeds that of the calcium chloride, although but little. There is thus no apparent relation between the flocculating power and the migration influence. One seems, however, reasonably justified in surmising that the migration influence stands in a fairly direct relation to some function
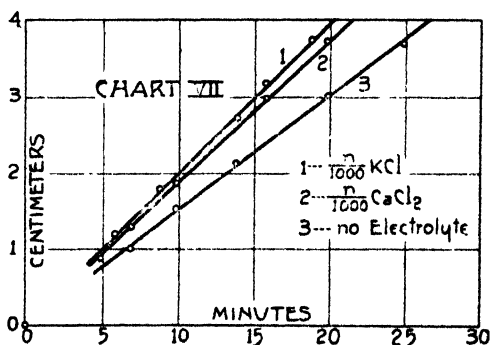
of the concentrations of the electrolyte added, very possibly the conductivity. In this event the acceleration of the migration rate would be represented by $S.K.\lambda$ where K is the original rate of the uninfluenced sol and λ the conductivity induced by the added electrolyte while S is a factor which varies with the condition of the particular sol, and is at present indeterminate. Before this principle can be established with any degree of definiteness, a far more exhaustive series of experiments is necessary. These are planned for the near future. As a matter of fact results of similar experiments performed some years ago by R. C. Pollock and F. S. Pratt on arsenious sulphide sols, the results of which are in preparation for publication, show a quite different relationship.

Effect of Hydrogen Sulphide.—It has been pointed out above that the effect of hydrogen sulphide is to reduce the rate of migration. Repeated measurements were made of this effect which was always found to occur, whether or not electrolyte were present. The results of some measurements of the effect are given in Chart VIII. The reduction of the
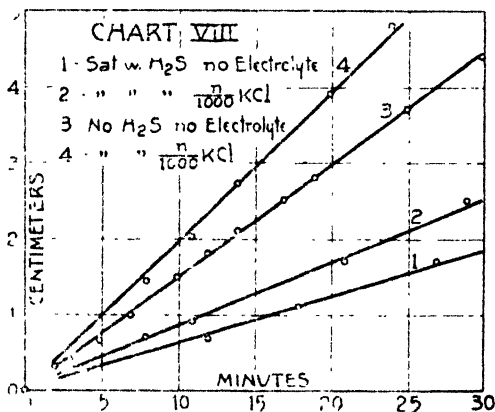
migration rate by hydrogen sulphide is found to be very large. The action in this case was found to be reversible, the migration rate increasing when hydrogen sulphide was dialyzed out and diminishing when it was resaturated with hydrogen sulphide.

Here again is found evidence of the rule that the influence of the electrolyte on the migration rate is closely proportional to the value of this quantity for the sol without electrolyte. The distances on Curve 2 are to those on Curve 1, taken at the same time as 1 : 1.35. Those on Curve 4 are to those on Curve 3 as 1 : 1.34. The different value for this ratio from that obtained from the same sol saturated with hydrogen sulphide illustrates the character of S in the formula suggested above.

Influence of Oxygen.—During the course of the investigation it was considered wise to determine whether or not free oxygen played any part in influencing the migration rate. The results were negative. Air or oxygen bubbled through a sol freed from hydrogen sulphide by dialysis showed not the least effect. If a sol saturated with hydrogen sulphide were used there occurred always an increase of migration rate which was restored to its original value by resaturation with hydrogen sulphide. If air or oxygen were passed through for a long time the migration rate took on a value very close to that of the dialyzed sol, from which it was concluded that the influence of the air or oxygen was merely that due to displacement of hydrogen sulphide.

Summary

Copper sulphide sols were prepared in a number of different ways and their conduct with respect to flocculation by electrolytes as well as their rates of migration in the electric field were studied. The following conclusions are indicated by the data obtained:

(1) The concentration of electrolyte necessary to flocculate in twenty-four hours is independent of the origin of the sol.

(2) It is within wide limits independent of the dilution of the sol.

(3) It is independent of the presence or absence of free hydrogen sulphide in the sol.

(4) The relative flocculating powers of the chlorides of potassium, calcium and aluminum are as 1 : 39 : 875.

(5) Evidence is found that sols which have been deprived of hydrogen sulphide are unstable, and will ultimately flocculate spontaneously. The time required is, however, very long, five or more months. Electrolyte additions show no difference in the conduct of sols saturated and those unsaturated with hydrogen sulphide (see 3).

(6) The rate of migration of these sols in the electric field is largely influenced by the origin of the sol.

(7) It is accelerated by the addition of electrolytes, but in a way which seems to bear no relation to the flocculating value of the electrolyte used.

(8) The acceleration of the migration rate depends upon the migration rate of the original sol, and seems fairly well represented by an expression of the form $S.K.\lambda$, where K is the migration rate of the original sol and λ a function of the concentration (perhaps of the conductivity) of the electrolyte added and S is a factor depending on some specific property of the particular sol used.

(9) Other conditions being kept constant, the migration rate is increased by dilution.

(10) The migration rate is greatly reduced by hydrogen sulphide, and increased by its removal, the effect being readily reversible.

(11) Bubbling air or oxygen through a sol containing hydrogen sulphide affects the migration rate merely by displacing hydrogen sulphide. Resaturation with hydrogen sulphide restores the rate to its original value.

A considerable portion of the experimental work involved in this paper was carried out at the laboratory of the College of the Pacific, College Park, Cal., the remainder at Stanford University.

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CHEMICAL COMPOSITION VERSUS ELECTRICAL CONDUCTIVITY

BY COLIN G. FINK

Some years ago, while still at the University, I carried out a number of experiments on the electrothermic production of ultramarine; powdered mixtures of sodium sulphide, china clay and carbon were interposed between carbon electrodes in a closed crucible furnace. I observed at that time that in order to keep the electrical resistance and the temperature of the charge fairly low so as to avoid decomposition of the ultramarine as soon as it was formed, it was necessary to use very finely divided carbon, such as lampblack. With charges made up of powdered coke which was coarse compared to the lampblack, I could not get any appreciable current to pass between the carbon electrodes up to potentials of 250 volts. Subsequently, I have found repeatedly that the electrical conductivity of mixtures of finely divided substances is a function of the relative size of the components.

Experimental

A series of tests was made in order to get values of a more quantitative nature. Two substances were selected, the physical properties of the one as divergent as possible from those of the other: a black metal powder, tungsten, and a white insulator powder, thoria. The advantages in this selection are manifold. Both tungsten and thoria will stand very high temperatures and can, therefore, be made practically moisture-proof. It is a well-known fact that in all high resistance tests adsorbed moisture is a very disturbing factor. As regards metals such as copper and silver, these were not serviceable since they cannot be heated to high temperatures without partial vaporization, which though slight is sufficient to cover the surface of the insulator granules with a highly conductive film. Other factors that decided our selection in favor of tungsten and thoria were: (1) High state of purity; (2) availability of both in extremely fine powdered form

(readily sifted through 250 mesh silk gauze); (3) constancy and stability under ordinary atmospheric conditions; (4) sharp distinction in color; (5) high specific gravities (which reduced the tendency to dust).

All mixtures here recorded were made up of equal weights of tungsten and thoria. As regards the size of the particles, the mixtures would pass readily through silk having 250 meshes to the inch. The holes in this silk are about 0.025 mm (0.001 ") in diameter. Attempts to segregate particles of a well-defined size by such methods as suspending in water, or in organic liquids or in air, were frustrated on account of the persistent tendency of the very fine particles to form agglomerates.

We finally resorted to the familiar "tap test," which gave us fairly good comparative values of the fineness of the various powders used. Ten grams of the powder or powder mixtures were filled into a 10 cc glass graduate and tapped to constant volume; usually after seven minutes, no further decrease in volume could be detected. The ultimate volume in cc divided by 10 gave us the relative volume (v_r) as recorded in Table I. It can easily be demonstrated that the values for v_r are a function of the density and mean particle size. At first there seemed to be a serious objection to the tap test, namely this, that a ThO_2 or a W powder composed of, say, equal parts of coarse and fine particles would give the same value for v_r as a second powder whose particle size was a mean between the two limiting sizes of the first powder. This objection to the tap test was automatically set aside since, in the ordinary preparation of metal or oxide powders in single small lots, by far the greater majority of particles are very nearly of the same size. This tendency to form a "standard" size is a universal phenomenon, the dimensions of any particular standard being dependent upon physical conditions such as temperature, strength of solution, etc., under which the particular powder is prepared. Compare, in this connection, the uniform size of the crystals of granulated sugar as regulated by the "strike pan."

Colin G. Fink

TABLE I

Mixture	Relative volume (v_r)				Appearance of mixture
	ThO$_2$	W	Mixture Found	Mixture Calculated	
R	0.720	0.113	0.430	0.417	White
P	0.720	0.350	0.565	0.535	White
Z	0.576	0.235	0.389	0.406	White
T	0.305	0.113	0.200	0.209	White
S	0.305	0.330	0.275	0.318	Black
X	0.238	0.577	0.420	0.408	Black

Referring to Table I, we note that the white thoria powders varied in relative fineness between 0.720 and 0.238 and the black tungsten powders between 0.577 and 0.113. In column 5 the calculated value for v_r of any mixture is equal to one-half the sum of the v_r values of the ThO$_2$ and W constituents. These calculated values agree fairly well with the experimental and support our contention that the particles of any freshly prepared powder are of fairly uniform size. If this were not the case no such agreement between the values of columns 4 and 5 would be possible. In the last column of the table is given the appearance of the mixture, whether nearly white or nearly black. If the v_r value for the white powder is high as compared with the v_r value for the black powder, the appearance of the mixture is white; if the white powder is coarser than the black powder, the appearance of the mixture is black. In other words, whenever the ratio of v_r for thoria to v_r for tungsten is greater than 2, the mixture is white and if less than 2 the mixture is black, where 2 is equal to the absolute density of tungsten (19.6) divided by the absolute density of thoria (9.8).

Electrical Measurements

The powders were pressed into rods 4 cm long and $\frac{1}{2}$ cm square. They were then placed in a tungsten-hydrogen furnace and fired at 1600-1650° for three hours. This firing caused the rods to sinter together, and rendered them practically proof against moisture. The fired rods were kept in a

P_2O_5 desiccator. The rods were then mounted between brass clamps and the resistance measured on a wheatstone bridge with a sensitive galvanometer. Care was taken to make these measurements on days when the humidity of the air was low.[1]

In view of the differences in "color" of the various mixtures in the powdered form, it was not very surprising to find marked differences in the electrical resistances although the firing at 1600°, however, resulted in an almost uniform shade for all of the mixtures. In Table II are recorded four of the characteristic resistance values found: In the last column are the calculated specific resistance values.

TABLE II

Powder	Resistance	Resistivity
ThO_2 No 2	Over 10^{12} ohms	Over 10^{12} ohms
Z	41.8	173.0
X	0 0271	0.108
W No. 1	0 0040	0 016

The powders, ThO_2 No. 2 and W No. 1, were pressed up into rods the same size as those of the mixtures; they were likewise fired at 1600° for 3 hours. Since in all of our original powders a small percentage of grains was present whose size was smaller than that of the majority of grains, our results would tend to show that under ideal conditions of mixture, relative grain size and uniform distribution, the resistivity values for white mixtures such as Z would be even higher than here recorded. Similarly, the resistivity values for black mixtures such as X would be lower than those found, approaching a limiting value equal to twice that of the 100 percent metal rod.

Conclusion

In general we may say that the electrical conductivity of a substance is primarily dependent upon the shape and the

[1] Compare in this connection H. L. Curtis: Phys. Rev., **3**, 490 (1914), "Surface Leakage over Insulators."

Colin G. Fink

distribution of the fundamental grains or particles composing the substance, and secondly, upon the presence or absence of thin films of secondary material enveloping these ultimate grains.

On the basis of this theory we can account for the comparatively high conductivity of gels that contain but a trace of conducting material.   We can also account for the marked difference in resistance of, for example, two samples of commercial copper whose chemical composition is identical, depending upon whether the impurity, such as sulphur, is uniformly dissolved in the metal or whether it forms a film ("cement") of copper sulphide around pure granules of copper. The latter case is to be regarded, as Bancroft suggested, as an emulsification of copper, in copper sulphide.   The high resistance of these surface films composed of, say, sulphide or oxide or arsenide accounts for the high resistivity values of copper when but a trace of the impurity is present.

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THE LUMINESCENCE OF THE IODIDE OF MILLON'S BASE

BY HARRY B. WEISER

The iodide of Millon's base, commonly called Nessler's precipitate, is obtained when Nessler's solution, an alkaline solution of mercuric potassium iodide, is treated with ammonia. According to Rammelsburg[1] and to Pesci[2] the structural formula of the compound is $N.Hg_2I.H_2O$, while Franklin[3] formulates it HOHgNHHgI. Physically the iodide is a chocolate-colored powder with a reddish brown tinge. Watts' Dictionary states that when heated the compound begins to give off water at 128°; heated more highly out of contact with air, it melts to a dark brown liquid and then decomposes. Roscoe and Schorlemmer[4] add that the decomposition is accompanied by the emission of light.

Since the majority of chemiluminescent reactions studied[5] have been those of combination or oxidation and not the reverse reactions of dissociation or reduction, it seemed desirable to investigate further the decomposition of the iodide of Millon's base to see whether the reaction emits light of a characteristic color and to add to the data previously obtained on mercury flames.

A quantity of the iodide was prepared by precipitating alkaline potassium mercuric iodide with ammonia. The precipitate formed was transferred to a Büchner funnel, washed until the wash water was neutral and finally dried in an oven at 115°.

A portion of the salt was placed in a tube and sealed to one of the exit tubes of a mercury-filled gas burette supplied

[1] Jour. prakt. Chem., (2) 38, 508 (1888).

[2] Zeit. anorg. Chem., 21, 361 (1899).

[3] Franklin: Jour. Am. Chem. Soc., 29, 35 (1907); cf. Hofmann and Marburg: Liebig's Ann., 305, 204 (1899).

[4] Roscoe and Schorlemmer: Treatise on Chemistry, 2, 692 (1907).

[5] Trautz: Zeit. phys. Chem., 53, 1 (1905); Bancroft and Weiser: Jour. Phys. Chem., 18, 213, 281, 762 (1914); 19, 310 (1915).

with a two-way stopcock. After evacuating the tube containing the iodide, it was slowly heated and decomposition took place. Qualitative analysis of the gas evolved showed it to consist of nitrogen and ammonia. Some ammonium hydroxide was formed by the union of ammonia with water vapor which was also a product of the action. Mercuric iodide and metallic mercury condensed on the tube above the heated portion. Contrary to the statements found in the handbooks, the decomposition of the compound took place without previous melting. Numerous attempts were made to fuse the compound, even heating it in a sealed tube under pressure, but all were unsuccessful. It was frequently observed that when a quantity of the salt was slowly heated in a test-tube, that the mercuric iodide formed in the decomposition condensed on the tube above the heated salt and when the temperature was raised fused to a red-brown liquid. It seems probable that this may have been mistaken for fusion of the undecomposed iodide of Millon's base.

A portion of the salt was heated in a test-tube immersed in a paraffine bath and an evolution of ammonia was detected with moist litmus paper at a temperature of 160°. The velocity of decomposition increased slowly with rising temperature but the critical reaction velocity necessary for the production of light was not reached until above 350°. In this respect the decomposition of the iodide is similar to the thermal decomposition of a number of exothermic compounds, *c. g.*, HgO, which begins to give off oxygen very slowly at as low a temperature as 175°[1] but does not undergo rapid decomposition until heated to redness.

The light emitted by the reaction is particularly bright so that it may be readily seen even in daylight. It furthermore possesses a distinctly characteristic color that at first reminded me of the violet potassium flame. On comparing the two colors it was found that the luminescence produced by the decomposition of the iodide was a darker, more distinct violet unmixed with the red luminescence that modifies the

[1] Schoch: Am. Chem. Jour., **29**, 319 (1903).

violet of the potassium flame. On first observation it was thought that the violet light might be due to the presence of potassium iodide adsorbed by the precipitated salt. Although spectroscopic examination failed to disclose any of the characteristic lines of the potassium flame, a further test was carried out with the iodide precipitated from an alkaline solution of mercuric sodium iodide thereby removing any possibility of the presence of potassium. The decomposition of the 'odide so prepared produced the same characteristic luminescence.

The question naturally arose whether this luminescent react'on is exothermic or endothermic. It is a well-known fact that in the majority of cases the thermal decomposit:on of a dry compound is attended by the absorption of heat. In some cases notably in explosive reactions and in the decomposition by heat of potassium chlorate and potassium bromate the decomposition is accompanied by an evolution of heat. Even when thrown onto a hot plate considerably above the decomposition temperature of the iodide the rapid decomposition can no more be regarded as explosive in character than the rapid decomposition of potassium chlorate which evolves heat or the rapid decomposition of silver oxide or potassium iodate which absorbs heat. This led to further study to determine whether the thermal effect was s:milar to that of most decomposition reactions or whether the decomposition was accompanied by an evolution of heat like potassium chlorate.

In order that a reaction may be accurately studied thermochemically it must take place rapidly at ordinary temperatures and must proceed rapidly to the end. If a reaction takes place rapidly only at elevated temperatures, it enormously complicates the accurate determination of the thermal effect and if the thermal effect is not particularly marked it even renders the determination of the heat sign a difficult procedure.

Attention has already been called to the fact that the decomposition of the iodide of Millon's base does not proceed with any great rapidity until around 400° or above the range

of use of an ordinary mercurial thermometer.   It was thought,
however, that the slow decomposit'on at a lower temperature
might be accompanied by sufficient thermal effect so that the
heat sign could be measured with an accurate thermometer.
To try this an electric oven was heated to approximately 230°.
By keeping the oven out of the region of air currents and by
surrounding the thermometers with an asbestos jacket, a
fairly constant temperature could be maintained that was
read on a thermometer graduated in tenths of a degree.   The
bulb of a Beckmann thermometer was placed concentrically
in a thin-walled test-tube and to hold it in place was sur-
rounded with powdered barium sulphate.   The tube was
supplied with a cork which fitted the opening in the top of
the oven and served to hold it firmly in the heated air.   After
waiting for more than an hour for the temperature to become
constant the Beckmann was read.   The thermometer was
then surrounded with the iodide and the procedure repeated.
Repeated attempts gave unsatisfactory results.   Because of
the inability to maintain the temperature absolutely constant
at so high a temperature with the apparatus at hand, the read-
ing on the Beckmann fluctuated during a long period of time
through a few tenths of a degree, showing no marked tendency
in either direction.

It seemed likely that the best results could be obtained
by bringing about rapid decomposition of the iodide in a con-
fined space and noting the effect on a thermometer the bulb

Various devices were made and tried out to utilize the
heat of an electrically heated wire in a water calorimeter for
effecting the decomposition of the salt and measuring the
comparative rise in temperature of the water when a given
quantity of the current was passed, with and without the pres-
ence and accompanying decomposition of the salt.   Be-
cause of the slight thermal effect of the reaction compared
with the heat of the current and because of the difficulty in
correcting for the quantity of heat necessary to raise the salt
from room temperature to the temperature of rapid decomposi-
tion, the method was found to be impracticable.

It seemed likely that the best results could be obtained
by bringing about rapid decomposition of the iodide in a con-
fined space and noting the effect on a thermometer the bulb

of which was suspended in this space. A description of the apparatus that was finally constructed for this purpose and the method of manipulating it in the specific case of the decomposition of the iodide are as follows: A Hoskins' crucible furnace was connected with the source of current through a slide wire rheostat and regulated so that 1.8 amperes passed through the furnace. The furnace was allowed to heat until its temperature had become approximately constant, after which a 500 cc round bottom flask supplied with a two-hole stopper was set snugly over the circular opening in the furnace and was clamped firmly in place. In one hole of the stopper was placed a thermometer, graduated from 100° to 220° in tenths of a degree and in the other hole was placed a glass tube of 3 mm bore, on the lower end of which was blown a thin-walled bulb that contained the 1-gram sample of the iodide. A glass rod of suitable length was placed in the bulb for the purpose of breaking the bulb and releasing the salt at the desired time. Over the end of the bulb tube was placed a short piece of narrow rubber tubing that fitted the glass rod snugly. A short slit was cut in the rubber tubing making a Bunsen valve. The bulb of the thermometer was placed 4 cm from the bottom of the flask and was held firmly in place by a burette clamp. At the outset of the experiment the bulb containing the iodide was placed at the same level. For protection from air currents the entire apparatus was surrounded by a jacket of asbestos with a glass window in front, through which could be observed the thermometer reading and the reaction within the flask. When the thermometer was placed in the position above described and when the current passing through the furnace was 1.8 amperes the thermometer stood around 180°. When a constant temperature was obtained the bulb of salt was lowered until it was about 0.5 cm from the bottom of the flask and the thermometer was read after waiting until temperature equilibrium was restored. By a gentle tap, a hole was punched in the bottom of the bulb releasing the salt. By this procedure the salt was first heated to a temperature not far from the point of rapid de-

composition and the bottom of the flask was such a temperature that the heated salt dropping on it immediately started to decompose with the emission of light. In a score or more of experiments carried out to secure the best conditions for the complete, rapid decomposition of the salt, the thermometer dropped from 3 to 5 degrees in the few seconds during which the reaction proceeded.

For securing the best results certain precautions other than those mentioned should be observed: It is undesirable to have the temperature of the bottom of the flask too high since the decomposition at the point of contact with the flask will be so rapid that the evolved gases will puff a large portion of the salt from the heated region. This also tends to fan up around the thermometer bulb, the more highly heated air in the bottom of the flask. For the same reason it is likewise best not to have the iodide precipitated on the bottom of the flask all at once but instead to have it run from the broken bulb in a stream, requiring a few seconds for emptying it completely. This is readily accomplished by breaking the bulb and then *gently* tapping the top of the bulb tube.

The thermometer dropped rapidly during the decomposition. This was followed by a short period of constant temperature and then by a uniform rise. Since the walls of the flask were coated with mercury and mercuric iodide which acted as a heat insulator, the thermometer naturally rose somewhat higher than the point at which it stood before the breaking of the bulb.

A logical objection may be raised to the result of this experiment, namely, that the condition in the flask which brought about the fall of the thermometer was not caused by the negative thermal effect of the reaction but instead was due to the quantity of heat necessary to raise the temperature of the salt from a point slightly under the temperature of rapid decomposition up to the point of rapid decomposition. A part of the lowering was unquestionably due to the latter effect but it seemed scarcely likely that this was the important thing. Even if we grant that the heat necessary to raise the

heated salt to the temperature of rapid decomposition was sufficient to cause an appreciable lowering of the thermometer, the subsequent rapid decomposition, if it evolved heat, would cause it to rise or at least would slow down the rate at which it dropped. Observation showed that exactly the opposite was true.

It was found impossible to find a suitable substance with which to run a "blank" test, obviously because there is no substance which, when treated as the iodide was, would behave in a similar way without chemical action and corresponding heat changes coming in. However, a test was made to determine the effect on the thermometer when barium sulphate, an infusible, non-volatile substance was substituted for the iodide in the experiment above described. The procedure followed was identical with that above given as the best conditions for decomposing the iodide. It was found that the thermometer fell very slowly about 0.6 of a degree and then began to rise. Since decomposition of the iodide takes place at a lower temperature than that of the bottom of the flask and since the specific heats of the iodide and barium sulphate can not be very widely different, it is evident from the above experiment that the fall of the thermometer during the decomposition of the iodide cannot be accounted for solely by the difference in temperature between the iodide before breaking of the bulb and that at which the salt undergoes rapid decomposition. Of particular importance should be mentioned the additional fact that even the relatively slight lowering with barium sulphate was gradual and occupied a much longer time than the much greater lowering during the decomposition of the iodide.

To test the apparatus, the decomposition of certain compounds was carried out, the heat sign of which was known. A mixture of potassium chlorate and manganese dioxide in the proportion of about 3 to 1 caused the thermometer to rise from the start. Like results were obtained with ammonium nitrate. With silver oxide which absorbs a small amount of heat on decomposition, a slow fall in temperature was noted

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as long as the relatively slow decomposition took place, after which it rose gradually. That this fall in temperature was not due altogether to the quantity of heat necessary to raise the residue of silver to the temperature of the bottom of the flask, the experiment was repeated with the residue of silver alone. The fall in temperature was appreciably less.

In the light of these experiments we are led to the conclusion that the decomposition of the iodide of Millon's base with emission of light is accompanied by a negative thermal effect. Attention should be called to the fact that the temperature necessary for securing sufficiently rapid decomposition to obtain light is above the vaporization temperature of the reaction products.

The result of this investigation is important as an illustration of the fact that the thermal effect of a luminescent reaction is not necessarily positive. The result is merely illustrative of what *must* be true in a number of cases, since a number of luminescent reactions are already known that are accompanied by an almost imperceptible temperature change and since it is probable that all reactions emit light providing the reaction velocity is sufficiently high.[1] That this reaction is further important as an illustration of the feasibility of obtaining light is evident from the following quotation from Bancroft:[2] "To obtain cold light one must find a reaction which can be made to go rapidly, which *absorbs heat*, or evolves but a small amount of heat and which has a high conversion factor for light."

Luminescent Reactions of Mercury

Investigation of flame reactions in which the element mercury is involved, discloses the presence of at least three characteristic and more or less separate and distinct luminescences: orange, green and violet.

The orange luminescence: An orange luminescence is ob-

[1] Bancroft: Jour. Franklin Inst., **175**, 129 (1913).
[2] The Theory of Cold Light: Trans. Ill. Eng. Soc., **10**, 289 (1915).

tained when cathode rays act on a mercurous salt,[1] when mercury is made anode in the electrolysis of a chloride, bromide or iodide solution[2] and near the mercury surface where mercury is in excess, in the combustion of the element in chlorine or bromine. The latter is best observed when just the surface of the mercury is uniting with the halogen with the emission of light rather than when a large flame is investigated.

Since in all of the above reactions the chief product is mercurous salt the reaction which produces the orange luminescence is the reaction from mercury to mercurous ion or mercurous salt. Inasmuch as the orange luminescence is not so marked in the spark spectrum of the element *in vacuo*, it is probable that the orange light is due chiefly to the reaction,

$$Hg^{\cdot} \longrightarrow \text{Non-dissociated mercurous salt.}$$

The green luminescence: A green or greenish yellow luminescence is obtained when cathode rays act on mercuric chloride or bromide,[3] when mercury burns in an excess of chlorine and in the electrolysis of concentrated sulphuric acid with a mercury anode.[4] Under these conditions the mercuric salt is formed chiefly but the reaction does not take place to the exclusion of or without the intermediate formation of the mercurous salt. Hence whatever the color of the light emitted during the formation of mercuric salt from mercury, the color will necessarily be modified to a greater or lesser extent by the orange luminescence.[5] In all the experiments on direct union which result in the formation of the mercuric salt, a green luminescence is obtained that is modified by the orange to such an extent that the color is best described as greenish or as greenish yellow. When mercury is burned in bromine, the orange light near the mercury surface where

[1] Wilkinson: Jour. Phys. Chem., **13**, 691 (1909); Farnau: Ibid., **17**, 637 (1913).

[2] Wilkinson: Loc. cit.; Bancroft and Weiser: Jour. Phys. Chem., **18**, 762 (1914).

[3] Farnau: Loc. cit.

[4] Wilkinson: Ibid.

[5] Cf. Bancroft and Weiser: Jour. Phys. Chem., **18**, 281 (1914).

mercury vapor is in excess is so bright that the body of the flame where mercuric salt is formed chiefly, appears distinctly yellow to the unaided eye. The tendency is in the right direction and is exactly what we should expect under the circumstances.

It is probable that the light emitted during the electrolysis of concentrated sulphuric acid with a mercury anode is due in part at least to a silent discharge.[1]

The green luminescence unmixed with the orange cannot be secured, as might be expected, by burning mercurous chloride or bromide in an excess of the halogen since the heat necessary to cause a sufficiently rapid reaction to emit light causes the readily decomposed mercurous salt to dissociate into its elements. In consequence the color of the emitted light is the same as that obtained by burning mercury in the halogen.

Inasmuch as the green luminescence is marked in the spark spectrum of the metal even in vacuum, it is probable that the green luminescence is due chiefly to the reaction $Hg^{\cdot} \longrightarrow Hg^{\cdot\cdot}$. What light if any is due to the reaction from mercuric ion to mercuric salt has not been determined.

The violet luminescence: Attention has been called to the remarkably distinct violet luminescence obtained during the decomposition of the iodide of Millon's base. Since metallic mercury is one of the decomposition products of the salt it seems probable that a part at least of the violet luminescence is produced by the reaction $Hg^{\cdot\cdot} \longrightarrow Hg$. This seems all the more probable in view of the fact that the violet luminescence is marked in the spark spectrum of mercury.

The results of this paper may be summarized as follows:

(1) The iodide of Millon's base decomposes on heating with the formation of ammonia, mercuric iodide, nitrogen, water and mercury. Ammonia is evolved at as low a temperature as 160° but the decomposition is not rapid until about 400°. The decomposition takes place without previous melt-

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[1] Wilkinson: Loc. cit.; cf. W. von Bolton: Zeit. Elektrochemie, **9**, 913 (1903).

ing. Under the conditions of rapid decomposition, the reaction emits light and absorbs heat.

(2) The light emitted by the decomposition of the iodide of Millon's base is particularly bright and is of a distinct violet color.

(3) A summary of the luminescent reactions of mercury has been given.

(4) The reaction of mercury to mercurous salt gives an orange luminescence; of mercurous salt to mercuric salt a green luminescence; and of mercuric salt to mercury a violet luminescence. It is probable that the orange luminescence is due chiefly to the reaction $Hg^{\cdot} \longrightarrow$ nondissociated mercurous salt, the green luminescence to the reaction $Hg^{\cdot} \longrightarrow Hg^{\cdot\cdot}$ and the violet luminescence to the reaction $Hg^{\cdot\cdot} \longrightarrow Hg$.

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HEAT OF DILUTION OF ALCOHOL IN BENZENE

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I. Heat of Dilution and Its Relation to Abnormal Molecular Weights

The heat of dilution of alcohol in benzene was measured by Walker and Henderson[1] in an investigation including several other binary organic mixtures.

Walker found a marked absorption of heat when solutions of alcohol in benzene were diluted. His observations were made at a temperature in the neighborhood of $16°$ C and he did not study the effect of temperature.

Bancroft[2] discussed the general bearing of the heat of dilution of solution on the observed molecular weight of the substance dissolved in the solvent in question. The points brought out in that paper are of such general interest and, at the same time, so often overlooked that a brief résumé may not be out of place.

The equation of van't Hoff[3] is

$$PV = RT \frac{N}{n} \log \frac{p_0}{p'}.$$

where P = osmotic pressure; V = volume through which a semipermeable piston moves in squeezing out that amount of solvent in which one molecular weight of the solute is dissolved; R = the gas constant; T = the absolute temperature; N/n = gram molecules of solvent per gram molecule of solute (the molecular weights are those of the solvent in the vapor and of the solute in the solution); p_0 = the vapor pressure of the pure solvent at the temperature T; p' = the partial pressure of the solvent in the solution at the temperature T. This equation is independent of any assumption in regard to the heat of dilution.

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[1] Trans. Roy. Soc. Canada, 8 III, 105 (1902).

[2] Jour. Phys. Chem., 10, 319 (1906).

[3] Kgl. Svenska Vetenskaps Akademiens. Handlingar, 21, 3 (1886); Zeit. phys. Chem., 1, 483 (1887).

If we assume that $PV = RT$, the preceding equation simplifies to

$$\frac{n}{N} = \log \frac{p_0}{p'}$$

which is the van't Hoff-Raoult formula and is the basis of our methods of determining molecular weights in solution.

The equation $PV = RT$ holds only in case the heat of dilution is zero and in case the degree of association or dissociation of the solute does not change with varying concentration. It is customary to attribute all variations to an actual change in molecular weight and to ignore the effect due to the heat of dilution.

In Bancroft's paper it was pointed out that for any given concentration we could apparently always postulate the relation

$$PV = Q + T \frac{d(PV)}{dT}$$

where Q is positive if heat is evolved when the solution is diluted. This equation can be integrated if we know Q as a function of T. When Q is zero, we have

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} = \text{const.}$$

and experiments show that the particular solution $PV = RT$ is the right one. When Q is independent of the temperature and is equal to the constant A we have the expression

$$\frac{P_1 V_1 - A}{T_1} = \frac{P_2 V_2 - A}{T_2} = \text{const.}$$

Adopting the same solution as before we obtain the equation

$$PV = RT + A$$

which can then be substituted in the original van't Hoff equation. If we make the assumption that

$$Q = A - BT$$

where A and B are constants, and if we solve as before we obtain the equation

$$PV = RT + A + BT \log T.$$

The heat of dilution which applies in these equations, and which we will call Q_H, is the heat effect observed when N/n molecular weights of the solvent are added to an infinitely large mass of the solution.   This heat effect cannot be measured directly but may be calculated from the equation

$$Q_H = \frac{\delta Q}{\delta \frac{N}{n}} \cdot \frac{N}{n}$$

where Q is the molecular heat of dilution obtained by diluting to the concentration N/n.   It is positive when heat is evolved on dilution.

Bancroft showed that the abnormal molecular weights for sodium in mercury and for sulphuric acid in water were eliminated if a correction was made for the heats of dilution which were independent of the temperature in these two cases. With alcohol in benzene, however, the heat absorbed when the solution is diluted is so great that the correction, when applied to the values found by Beckmann,[1] gives negative molecular weights, an absurd result.   This may mean that a temperature coefficient must be taken into account, or that something has been overlooked in the deduction.

II. Theoretical Effect of Temperature on Heat of Dilution

It follows from the first law of thermodynamics that the temperature coefficient of the heat of dilution will be zero if the heat capacity of the mixture is the same as the sum of the heat capacities of its components taken separately, that is, if it can be calculated linearly.   In every other case the heat of dilution will vary with the temperature.   This relation is given by Nernst.[2]

$$K_0 - K = \frac{U_{T+t} - U_T}{t}$$
$$= \frac{dU}{dT}$$

where K_0 is the original heat capacity, K the heat capacity

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[1] Zeit. phys. Chem., **2**, 728 (1888).
[2] Theoretical Chemistry, 6th Ed., pp. 9, 161.

after mixing, U_{T+t} and U_T the heat effects obtained by mixing at the temperatures $T + t$ and T, respectively. For small temperature differences the right hand expression may be written dU/dT, or using the notation employed elsewhere in this paper

$$K_o - K = \frac{dU}{dT} = \frac{dQ}{dT}.$$

This enables us to calculate the temperature coefficients of the heats of dilution of a pair of liquids if the heat capacities for various proportions are known. In most calorimetric measurements the temperature is not kept constant throughout each experiment, nor from one experiment to another.

It was thought that the measurement of the heat of dilution of alcohol in benzene at different temperatures might afford interesting results as an illustration of the above-mentioned effects of temperature on the heat of dilution, and also on account of the abnormal molecular weights of alcohol in benzene.

III. Apparatus for Measuring Heat of Dilution at Various Temperatures

The apparatus used in the experiments was what might be called an isothermal calorimeter, similar in principle to those used by Heselius,[1] Waterman,[2] and Cady.[3] The principle is to keep the calorimeter at a fixed temperature during the mixing, by adding or withdrawing a known amount of heat, depending on whether mixing is accompanied by absorption or evolution of heat. In this way we minimize errors by radiation, particularly those due to changes in temperature on mixing, and we avoid a correction for water equivalent. Since we are working at a fixed temperature, we eliminate the effect of changing temperature on the heat of dilution, and make unnecessary the determination of the specific heats of the various liquid mixtures. Since it was desired to measure the heat

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[1] Jour. de Physique, **7**, 499 (1888).

[2] Phil. Mag., (5) **40**, 413 (1895); Phys. Rev., **4**, 161 (1896).

[3] Jour. Phys. Chem., **2**, 562 (1898).

of dilution at 10°, 20° and 30° C, respectively, suitable thermostatic baths were provided to enclose both the calorimeter and the vessel containing one of the liquids to be mixed.

The calorimeter vessel was a Dewar tube, A, about 4″ in diameter and 8″ deep, internal measurements. In this a copper cup or tube, B, about $1\frac{1}{2}$″ in diameter and 5″ deep was set. The cup rested upon a wooden block. A stirrer moving perpendicularly operated inside this cup, and another similar stirrer in the space between it and the glass wall. A thermometer reading directly to 0.01° C was held in the outside space between the copper tube and the wall of the Dewar. The calorimeter vessel was closed by two corks, one above the other. One cork was bored to hold the copper tube B, and both corks were provided with the necessary holes for the passage of the stirring apparatus, thermometer and solvent inlets. The upper cork was even with the mouth of the Dewar, and both corks were held together by wide glass tubes passing through the holes for stirrers, thermometer, etc. In addition, a hole in the center of the upper cork allowed warm water to be run into the copper tube.

The dilution vessel D consisted of a large separatory funnel, inclosed in an inverted bell-jar. A thermometer reading to 0.02° C was held in the interior of the dilution vessel. The latter, with its water jacket, was held at a fixed height above the table, but could be swung in position over the calorimeter vessel as desired.

Both calorimeter and dilution vessel were surrounded by electrically controlled thermostatic baths of the type described by Morgan.[1] These allowed a regulation of temperature to within a few hundredths of a degree.

The water bath E provided a supply of water at a temperature slightly above that at which the experiment was to be run, the temperature of this bath being regulated by a gas burner connected to a thermo-regulator. The outlet of the water bath E was made as large as possible and held

[1] Jour. Am. Chem. Soc., **33**, 344 (1911).

Fig. 1
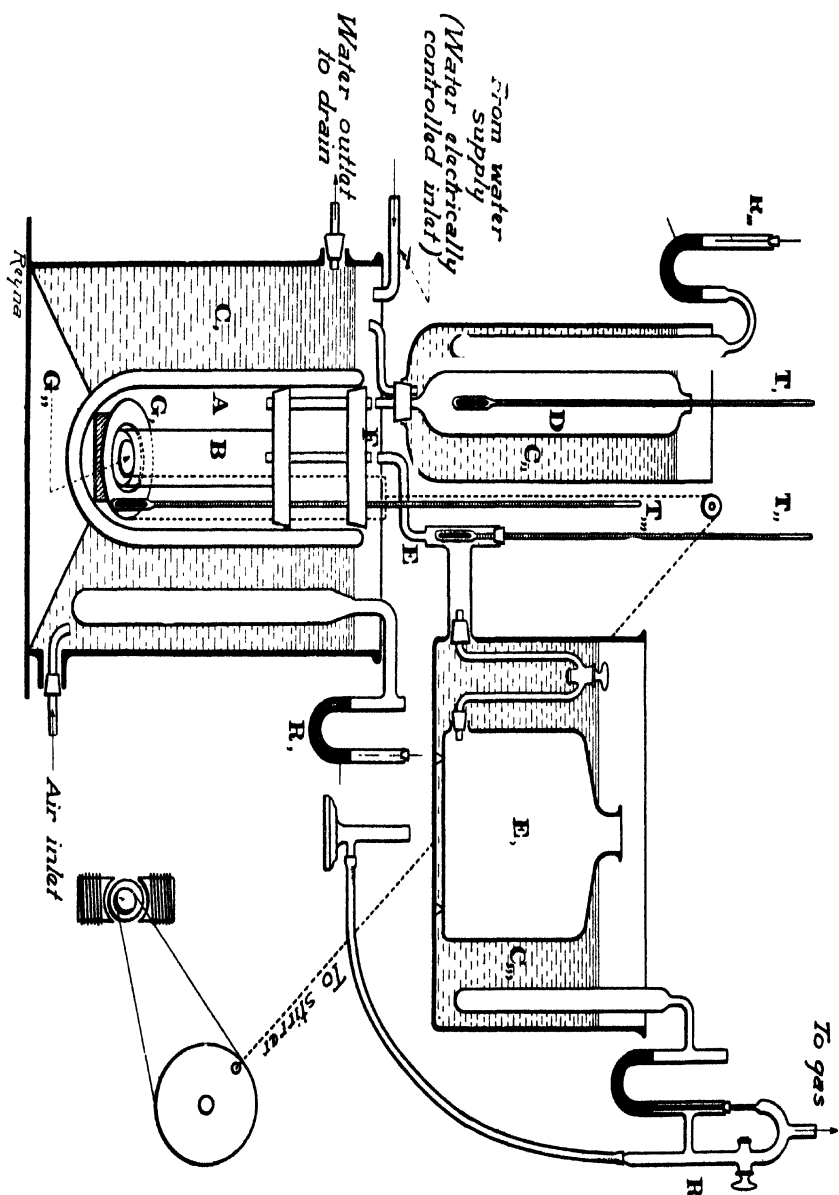
a thermometer reading to 0.02° C. The glass delivery tube leading from the outlet containing the thermometer could be swung through a wide arc so as to deliver water of known and constant temperature through the cork into the copper tube B, or into the waste pipe as desired.

The operation of the apparatus was as follows:

The thermostatic baths around the dilution vessel and calorimeter were set at the desired temperature. A weighed amount of benzene was introduced into the dilution vessel D, and a weighed amount of a known mixture of alcohol and benzene which was to be diluted was put in the Dewar bulb A. Copper tube B was weighed and put in place in the Dewar. The water in the bath E was heated and maintained at a temperature a few degrees higher than that in the other vessels, and the water allowed to run out through the outlet in which the thermometer was placed through the delivery tube into the drain.

The stirrers were set in motion and when the liquids in the dilution vessel and calorimeter were at exactly the same temperature (*i. e.*, the temperature of the baths surrounding these vessels), the benzene was run into the calorimeter mixing with the solution in the latter. At the same time the temperature of the water running from the water bath E was read and water was run into the copper tube B in the calorimeter, in sufficient amount to maintain practically constant temperature in the calorimeter.

The tube B was then removed, its outside carefully dried, and the tube and water weighed. The weight of the water multiplied by the difference in temperature between the bath E and the calorimeter vessel gave the number of calories absorbed in diluting the solution in the calorimeter.

For the most part the only correction needed was for the heat added by the stirring. This was found by observing the time required for the experiment, starting with the addition of benzene and ending with the final addition of water for the establishment of the original temperature. The heat effect of the stirrer was found by a blank experiment run on a mixture of known heat capacity.

TABLE I

Heat of Dilution at 10° C.   T — 10° = ΔT

No. of expt.	Observations						Calculations				
	Calorimeter		Added gr benzene	Time	Water added = W	Temp of water = T	Correction (cal)	Obs heat of dil. WXΔT	Cor. heat of dil. = q	$\dfrac{N}{n}$	Mol. heat of dil. = Q
	Gr alcohol 1	Gr benzene 2	3	4	5	6	7	8	9	10	11
1a	162.7	0	143.98	6'45"	40.14	22.57	6	504.56	510.6	0.52	144
b	162.7	0	143.98	7'	49.18	20 56	—9	519.34	510.34	0.52	144
2a	87.6	86.1	150	6'	42.29	20.1	0	427.12	427.12	1.59	368
b	94.6	93 1	166	7$\frac{1}{2}$'	54.84	18.86	0	485 8	485.8	1.62	376
3a	40.6	109.5	145	6'20"	35.34	17.99	0	282	282	3.69	695
b	40.6	109.5	145	6'	39.74	17.62	0	302.8	302.8	3.69	719
4a	27.6	172.4	100	2'30"	14	19.29	1.5	130	131.5	5.82	926
b	27.6	172.4	100	4'45"	16	19.41	—7.2	150.5	143.3	5.82	946
5a	13.8	136.2	150	4'45"	22.3	17.05	—13.5	157.2	143.7	12.25	1415
b	13.8	136.2	150	5'15"	19.8	17.46	1	147.7	148.7	12.25	1432
6a	6.9	143.1	150	5'15"	19.3	20.93	0	101.6	101.6	25.1	2100
b	6.9	143.1	150	3'15"	9.3	20.89	0	101 2	101.2	25.1	2097
7a	3.45	146.55	150	3'15"	5.2	20 05	1	52.25	53.25	50.8	2808
b	3.45	146.55	150	1'30"	4 3	20 09	5	43.4	48.4	50.8	2743
8a	1.72	148.4	150	2'15"	3.2	17.04	—3.6	22 52	18.92	102	3279
b	1.72	148.4	150	1'30"	3	17.01	—2.4	21	18.7	102	3275

Since heat is absorbed on dilution the values in Columns 8, 9 and 11 are negative.

TABLE II

Heat of Dilution at 20° C.   T − 20° = ΔT

No. of expt.	Observations						Calculations			
	Calorimeter		Added gr benzene	Time	Water added = W	Temp. of water = T	Correction (cal.)	Obs. heat of dil. = $WX\Delta T$	Cor. heat of dil. = q	$\frac{N}{n}$	Mol. heat of dilution = Q
	Gr of alcohol	Gr of benzene									
	1	2	3	4	5	6	7	8	9	10	11
1a	108.47	0	95.99	5'55"	49.1	29.30	14.7	456	470.7	0.52	202.5
b	108.47	0	95.99	5'35"	41.56	30.92	14	453.7	467.7	0.52	199
2a	58.4	57.37	100	6'30"	40.94	28.16	16	334	350	1.59	497
b	58.4	57.37	100	8'	71.34	24.90	8	349	357	1.59	502
3a	58.4	157.37	100	8'08"	42.12	25.23	24	220	246	2.59	693
b	58.4	157.37	100	7'	40.49	25.62	17.5	227.5	245	2.59	692
4a	18.5	81.5	100	5'50"	23.67	25.82	15	137.7	152.7	5.79	1073
b	18.5	81.5	100	4'	34.37	24.44	10	152.6	162.6	5.79	1096
5a	18.5	181.5	100	5'	21.52	25.13	12.5	100.4	123	8.97	1400
b	18.5	181.5	100	6'	32.34	23.3	15	106.7	121.7	8.97	1398
6a	6.16	93.82	150	6'45"	25.31	23.67	16.7	92.8	109.5	23.3	2217
b	6.16	93.82	150	7'	30.9	23.19	17	98.5	115.5	23.3	2261
7a	3.69	146.31	150	3'	10.63	23.11	7.5	33	40.5	47.3	2743
b	3.69	146.31	150	4'	17.75	22.2	10	39	49	47.3	2850
8a	1.848	148.15	150	1'	0.7	22.0	2 5	1.4	3.9	95.3	2893

Since heat is absorbed on dilution the values in Columns 8, 9 and 11 are negative.

TABLE III

Heat of Dilution at 30° C.   T — 30° = ΔT

No. of expt.	Calorimeter		Observations					Calculations			
	Gr alcohol	Gr benzene	Added gr ben-zene	Time	Water added = W	Temp. of water = T	Correction (cal)	Obs. heat of dilution = WXΔT	Cor. heat of dilution = q	$\frac{N}{n}$	Mol. heat of dilution = Q
	1	2	3	4	5	6	7	8	9	10	11
1a	162.7	0	143 98	8'	98.6	38	—30	788	758	0.52	213
b	162.7	0	143.98	8'	78.2	40	—30	782	752	0.52	212.6
2a	79.5	70 +	150	8'	66 1	39.4	—30	621	591	1.63	554
b	79.5	70.4	150	8'	92.4	37 3	—30	674	644	1.63	585
3a	39.7	110 3	150	8'	59.8	37.1	—30	424	394	3.86	1025
b	39.7	110.3	150	8'	65.1	36.33	—30	412	382	3.86	1012
4a	19.87	130.15	150	8'	43.25	36.9	—30	298	268	8.32	1638
b	19.87	130.15	150	8'	45.4	36.2	—30	281	251	8.32	1599
5a	9.92	140.08	150	8'	32.7	34.65	—30	152	122	17.25	2184
b	9.92	140.08	150	8'	34	34.55	—30	154	124	17.25	2193
6a	4.96	145.04	150	8'	19.8	33.96	—30	78	48	35.10	2634
b	4.96	145.04	150	8'	24.1	33 58	—30	86.2	56	35.10	2708
7a	2.48	147.5	150	8'	23.4	32.64	—30	61.9	31.9	70.8	3263
b	2.48	147.5	150	8'	25.1	32.06	—30	50.4	20.4	70.8	3049

Since heat is absorbed on dilution the values in Columns 8, 9 and 11 are negative.

In general, the results of two experiments on mixtures of the same concentration check within twenty calories. The results were calculated to molecular quantities and are given in Tables I–III inclusive.

Working at 10° C as the temperature of the calorimeter it was found that more accurate results were obtained by maintaining the temperature of the bath C a little below 10° C. In this way the heat introduced by stirring, etc., in most cases was neutralized, making the correction very small.

Working at 30° C as the temperature of the mixing liquids it was found that there was a slight but constant loss by radiation, etc., in spite of the careful insulation of the calorimeter. The time of all the experiments in this series was 8 minutes, for which a correction of —30 calories was introduced, this correction being based on the results of blank experiments.

The mixture in Expt. 2 at 20° was slightly different from that resulting in Expt. 1 in this series. The corresponding value of Q was found by prolonging the curve from $N/n = 0.52$ to $N/n = 0.59$, the latter value representing the solution used in Expt. 2. The correction due to this difference in concentration was 20 calories.

While, as stated before, the values at high dilutions are likely to be inaccurate they are of interest in showing the considerable absorption of heat even with very dilute solutions. The bearing of this heat effect at high dilutions in the case of electrolytes is discussed by Bancroft.[1]

IV. Form of Heat of Dilution Curve

Julius Thomsen[2] found that the heat of dilution of sulphuric acid in water was represented by the expression

$$Q = \frac{1786ox}{x + 1.8}$$

where $Q =$ heat of dilution in gram calories, $x =$ gram molecules of solvent (water) per gram molecular weight of solute.

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[1] Jour Phys. Chem., **10**, 319 (1906).
[2] Thermochemische Untersuchungen, **3**, 34.

An equation of this type does not represent the results given in Tables I–III.

A formula of the general type

$$x = \frac{bQ^2 + cQ}{Q - a}$$

where a, b and c are constants, was suggested by Professor Bancroft and found to represent the experimental results quite satisfactorily.

As we have already shown, when the heat capacity of the mixture is the same as that of the ingredients the heat of dilution for this case will be independent of temperature, or, in other words, the same for all temperatures. Whatever other conditions obtain at finite dilutions, at infinite dilution the heat capacities will be the same; that is, as infinite dilution is approached the temperature coefficient approaches zero. This means that the curves representing the heat of dilution at different temperatures will tend to unite at infinite dilution.

In the equation

$$x = \frac{bQ^2 + cQ}{Q - a}$$

it will be noted that when $Q = a$, $x = \infty$. Accordingly, we may replace the heretofore empirical constant a with the value of the heat at infinite dilution. Taking 3900 g calories for this value, which is probably not far from the truth, we have

$$x = - \frac{bQ^2 + cQ}{Q - 3900}$$

where b and c are constants, different for each temperature. Since heat is absorbed, the minus sign is used before the right hand expression above for clearness, the values of the constants changing accordingly. The latter may be determined quite simply by substituting the values of x and Q for two points on each of the three curves and solving the simultaneous equations obtained for each curve.

The observed and calculated values of Q for different values of x at 10°, 20° and 30° C are given in Table IV.

TABLE IV

CALCULATION OF HEAT OF DILUTION

By formula of type $x = \dfrac{bQ^2 + cQ}{Q - a}$

Heat of Dilution at 10° C

$$x = -\frac{0.0018Q^2 - 15.4Q}{Q - 3900}$$

$N/n = x$	Q_{Observed}	$Q_{\text{Calculated}}$	Difference
0.52	—144	—105	—39
1.59	—367	—336	—31
3.80	—709	—697	—12
5.85	—936	—965	+29
12.25	—1423	—1568	+145
25.00	—2099	—2210	+111
50.70	—2775	—2775	0
102.00	—3277	—3190	—87

Heat of Dilution at 20° C

$$x = -\frac{0.00387Q^2 - 9.76Q}{Q - 3900}$$

0.52	—200	—185	—15
1.59	—499	—465	—34
2.59	—691	—663	—28
5.79	—1084	—1128	+44
8.97	—1399	—1432	+33
23.30	—2240	—2190	—50
47.30	—2798	—2855	+57
95.30	—2893	—3167	+274

Heat of Dilution at 30° C

$$x = -\frac{0.0022Q^2 - 8.27Q}{Q - 3900}$$

0.52	—213	—216	+3
1.63	—570	—571	+1
3.86	—1018	—1010	—8
8.32	—1619	—1611	—8
17.25	—2189	—2210	+21
35.10	—2671	—2762	+91
70.80	—3206	—3200	—6

V. Temperature Coefficient of Heat of Dilution

The heats of dilution of alcohol in benzene at 10°, 20°
and 30° C are plotted in Fig. 2.

As will be seen from these curves, the variations in Q on either side of the 20° curve are roughly equal. This indicates that the heat of dilution varies linearly with the temperature, at any rate over the range included.

As stated in an earlier part of this paper, the effect of temperature on the heat of dilution has been shown to depend on the heat capacities of the liquids before and after mixing. If the heat capacities are the same, *i. e.*, if the specific heat of a
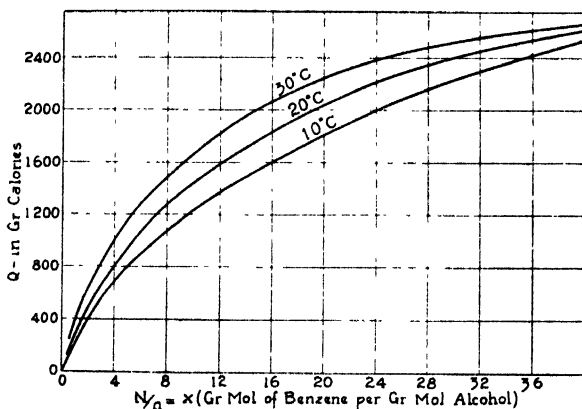
Fig. 2
Heat of Dilution of Alcohol in Benzene at 10°, 20° and 30° C
(Omitting highest dilutions)

mixture may be calculated additively from the specific heats of its components, the heat of dilution is independent of the temperature. Sulphuric acid in water is an example of this.

Walker and Henderson[1] have measured the specific heat of mixtures of alcohol and benzene. It may be of interest to calculate from their results what the temperature coefficient would be at various dilutions, and to compare it with the results of the experiments discussed in this paper. The data are given in Tables V–VI.

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[1] Trans. Roy. Soc. Canada, 8 III, 105 (1902).

TABLE V

Calculation of Temp. Coefficient of Heat of Dilution, from Specific
Heats of Alcohol and Benzene (Measured by Walker)

$N/n = x$	Sp. heat observed	Sp. heat calculated[1]	Heat capacity observed	Heat capacity calculated[1]	Difference in heat capacities $= \frac{\Delta Qx}{\Delta T}$
0.0	0.609	0.609	28.06	28.06	0
1.03	0.528	0.479	67.04	60.86	—6.18
1.585	0.511	0.460	86.89	78.28	—8.16
2.71	0.497	0.441	101.00	113.5	—12.5
6.2	0.460	0.423	243.4	223.6	—19.8
16.8	0.428	0.412	576.5	554.9	—21.6
33.7	0.417	0.408	1112.6	1092	—20 6
57.2	0.414	0.407	1864	1833	—31
86.2	0.410	0.406	2774	2750	—24
172	0.406	0.4057	5472	5468	—4
∞	0.405	0.405	∞	∞	0

TABLE VI

Calculation of Heat of Dilution at 10° and 30° C
Based on Experimental Results

$N/n = x$	Q at 20° observed	$\frac{\Delta Q}{\Delta T}$	Q at 30° C		Q at 10° C	
			Observed	Calculated	Observed	Calculated
0.52	—200	—3.2	—212	—232	—144	—168
1.59	—499	—9.0	—566	—589	—367	—409
2 59	—691	—12.4	—791	—815	—539	—567
5.79	—1084	—17.4	—1308	—1258	—915	—910
8.97	—1399	—19.8	—1645	—1597	—1200	—1201
23.12	—2240	—23 2	—2470	—2472	—2000	--2008
47.19	—2798	—23.5	—3140	—3033	—2450	—2563

If we plot the results, Fig. 3, in the last column, (V),
we find that they show a fairly smooth curve with the excep-
tion of one or two points, which may be out of place due to
experimental error. Considering that extreme accuracy was
not sought and that we are multiplying their actual results
to a much larger figure, particularly with more dilute solutions,

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[1] Calculated additively.

the result is very satisfactory. By drawing a smooth curve, as shown, we obtain a basis for calculating the effect of varying temperature on the heat of dilution.
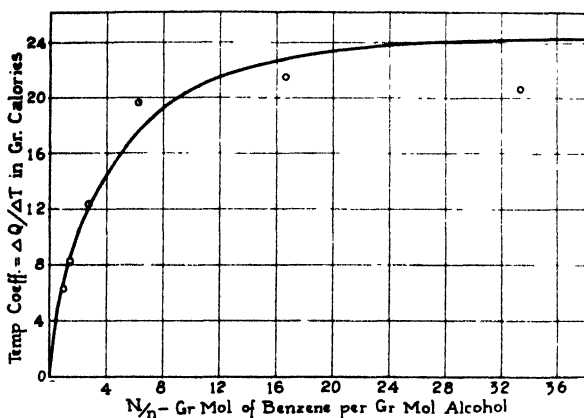
Fig. 3
Temperature Coefficient of Heat of Dilution of Alcohol in Benzene. Calculated from Specific Heats Measured by Walker and Henderson
Actual Observations—o

In Table VI, our experimental results at 20° C are taken as a basis and the values at 30° and 10° C, respectively, are calculated and compared with the observed.

The results, are, of course, only approximate, but show that the variations in heat of dilution with temperature are considerable and that the experimental differences are of the same magnitude as would be expected from the theory.

VI. The Influence of the Heat of Dilution on the Lowering of the Freezing Point

The molecular lowering of the freezing point for any solvent, which forms the basis of the molecular weight determination by the freezing-point method, is ordinarily taken as a constant quantity for any solvent. For dilute solutions, when there is no heat of dilution and the variation of the heat of fusion with temperature is negligible, van't Hoff gave the following relation:

$$E = \frac{RT^2}{100w}$$

where E is the constant for lowering of freezing point and is equivalent to the number of degrees lowering of freezing point produced by dissolving a gram molecule of the solute in 100 grams of the solvent; T is the absolute temperature of the freezing point; R = gas constant = 2 calories; w = heat of fusion of 1 gram of the solvent.

The heat of fusion of the solvent in the presence of a solution is different from that in the presence of the pure solvent, if there is any development of heat on diluting the solution. This question was discussed by Ewan[1] who gave the following equation for the relation between the relative vapor pressures of solvent and solution, the heat of fusion, the heat of dilution, and the lowering of the freezing point.

$$\log \frac{p_0}{p'} = \frac{1}{R}\left[\omega_0 \frac{T-T'}{T_0 T'} + \frac{dQ}{dX}\cdot\frac{T'-T}{TT'} - \frac{c}{2}\left(\frac{T'-T_0}{T'}\right)^2 \right.$$
$$\left. -\gamma\left\{ \frac{T-T'}{T}\cdot\frac{T-T'}{T'} - \frac{1}{2}\left(\frac{T-T'}{T}\right)^2 \right\} \right]$$

where p_0 = vapor pressure of pure solvent at T_0; p' = partial pressure of solvent in solution at T_0; R = gas constant in calories; T_0 = freezing point of pure solvent; T' = freezing point of solution, T_1 = temperature at which heat of dilution is determined; T = temperature at which osmotic pressure is to be determined; ω_0 is the heat of fusion of one gram molecule, of the pure solvent at T_0; $c = c_0 - c_1$; c_0 = heat capacity of one gram molecule of liquid solvent; c_1 = heat capacity of one gram molecule of solid solvent; $X = N/n$, N being the molecular weight of the solvent as vapor; dQ/dX = heat of dilution; $\gamma = NC_L$. The value of C_L is given by the equation

$$C_L = (1 + W)\frac{\delta C_l}{\delta W} + C_l - C_w$$

where W = grams of solvent per gram solute; C_l = specific heat of one gram of solution, and C_w = specific heat of one gram of solvent.

In recalculating the molecular weights, using Beckmann's

[1] Zeit. phys. Chem., 14, 409 (1894).

observations[1] for the depression (Δ) of the freezing point of benzene at different concentrations, we have used the following values:

$$C_w = 0.405$$
$$T = T_o = 278.5$$
$$\omega_o = 2360$$

The values of Q_H, determined by experiments described in this paper, were taken at the temperature $T_1 = 283$.

The values of C^l are taken by interpolation from Walker's[2] results, which as herein shown compared well with our results for the heat of dilution at different temperatures when reduced to the same basis. The values of $\frac{\delta C_l}{\delta W}$ were obtained graphically from the curve representing Walker's results.

Such data as are available indicate that there is no great difference between the specific heats of solid and liquid benzene, so the term involving these quantities, and representing the change of heat of fusion with temperature is neglected.

A little inspection of Ewan's equation will show that the net effect of the heat of dilution is as follows:

If the solvent melts in the presence of the solution, and heat is evolved on dilution of this solution, this heat will appear in addition to the heat of fusion, and will make the apparent heat of fusion abnormally large. This, in turn, will make the constant, E, abnormally small, and, since we have the relation

$$n = \frac{100 \, E}{W\Delta},$$

used by Beckmann, the molecular weight calculated thus will be too low; that is, if heat is evolved on dilution, the molecular weight calculated from the freezing-point lowering will be too low, on account of the heat of fusion being different in the case where there is a heat of dilution. When heat is absorbed on dilution the opposite is true throughout: the heat of fusion is too low, and the molecular weight too large.

[1] Beckmann: Zeit. phys. Chem., **2**, 728 (1888).
[2] Trans. Roy. Soc. Canada, 8 III, 105 (1902).

TABLE VII

Molecular Weight of Alcohol in Benzene

(Correcting for Effect of Heat of Dilution on the Lowering of Vapor Pressure)

$X = \frac{N}{n}$	W	C_1	γ	$\frac{\delta Q}{\delta X}$	T'	Δ	$\log \frac{p_0}{p'}$	Mol. weight observed (Beckmann)	Mol. weight revised (1)	Mol. weight revised (2). Assuming Q and $\gamma = 0$
1	2	3	4	5	6	7	8	9	10	11
1.82	3.09	0.503	4.71	—179	273.5	5.000	0.0822	318	308	323
2.61	4.41	0.492	3.26	—153	274.5	4.180	0.0691	265	256	270
4.02	6.80	0.476	2.08	—124	275	3.445	0.0555	208	207	216
6.66	11.80	0.459	1.44	—89.6	275.8	2.725	0.0436	159	158	164
10.11	17.10	0.446	0.811	—67.2	276.3	2.20	0.0349	128	131	134
16.92	28.70	0.428	0.475	—43.5	276.8	1.705	0.0270	100	100	102
25.80	43.60	0.421	0.202	—30	277.1	1.360	0.0212	82.5	84.5	85.7
54.20	91.90	0.414	0.046	—13.2	277.6	0.875	0.0135	60.9	62.9	63.6
119.5	202.10	0.4075	—0.17	—3.1	278	0.480	0.00705	50.4	54.6	54.2
359	608	0.405	0	—0.49	278.3	0.175	0.0027	45.9	47.5	47.5

The heat of dilution referred to here, in connection with the heat of fusion, is that caused by adding a gram of the solvent to a very large mass of solution of the concentration in question and is represented by $\frac{\delta Q}{\delta W}$, where W = the number of grams of solvent to one gram of solute.

If we calculate the value of $\log \frac{p_0}{p'}$, according to the equation of Ewan, we get a result similar to that discussed above with reference to the effect of heat of dilution on the molecular weight, calculated from the van't Hoff-Raoult formula:.

$$\log \frac{p_0}{p'} = \frac{n}{N}$$

The results of this calculation of the molecular weight allowing for the heat of dilution are given in Table VII. As will be noted, the results differ from those obtained by Beckmann (Table VII, Col. 9) for the following reasons:

(1) The presence of a negative heat of dilution tends to make Beckmann's values too high for the reasons above stated.

(2) The experimental value for E, used by Beckmann is 49, whereas the theoretical value calculated in the equation $E = RT^2/100W$ is 51. This will tend to make Beckmann's values too low by the same percentage throughout.

(3) The value $E = RT^2/100W$ is only true strictly speaking at infinite dilution where not only the heat of dilution but also the lowering of the freezing point are negligible as regards the total value of the absolute temperatures of the freezing point of the pure solvent and of the solut'on. As Ewan points out the true expression for E is

$$E = \frac{RT_0\,T'}{100\,W},$$

T_0 being the absolute temperature at which the solvent freezes and T' the absolute temperature at which the solution freezes. For very dilute solutions we have, of course, $T = T_0 = T'$, therefore,

$$E = \frac{RT^2}{100\,W}.$$

At more concentrated solutions where
$$T_o > T',$$
we have
$$T^2 > T_o T'$$
and the true value of E will tend to be less.   This effect tends to make Beckmann's values too high.

We see that factors (1) and (3) tend to make Beckmann's values too high, the error being proportional to the concentration, and becoming practically zero in each case at infinite dilution.   The second factor (2) tends to make all of his results somewhat low, but by the same percentage.   This composite correction produces the result noted in Column 10, Table VII, namely, that at high dilution the second effect is predominant, and our corrected values are higher than Beckmann's.   For instance, at $x = 359$, he obtained 45.9, and the corrected value is 47.5, of course. dQ/dW is negligible and $T = T_o = T'$, practically.   On the other hand at high concentrations factors (1) and (3) predominate, and make the corrected molecular weight lower than that given by Beckmann. This accounts for the apparent discrepancy between Columns 9 and 10, causing one to be lower than the other in some cases and higher in others.

Since we are not only interested in these corrected values, but also in noting the effect of heat of dilution, we have calculated molecular weights using the formula given by Ewan for log p_o/p', but making the deliberate assumption that Q and γ are equal to zero.   These values, found in Column 11, compared with those in Column 10 show the error caused by the effect of heat of dilution on the molecular lowering of the freezing point.

It must be noted that in all of the above calculations for the molecular weight, where we make allowance for the heat of dilution it is only as it affects the heat of fusion, and we make the explicit assumption that $PV = RT$, which is necessary for the relation
$$\frac{n}{N} = \log \frac{p_o}{p'}$$

to be true.   However, as already stated PV $=$ RT only when Q_H equals zero; otherwise a still further correction is needed before we arrive at the true molecular weight, as will be shown presently.

VII. The Effect of Heat of Dilution on Molecular Weight

As has already been shown in this paper, when $Q_H =$ a constant, A, and is independent of the temperature, we have for any fixed concentration the relation

$$PV = RT \pm A.$$

The sign $\pm$ is used to avoid confusion, the heat effect being taken as $+$ if heat is evolved on dilution.   In the particular case of alcohol and benzene in which we are now interested, heat is absorbed on dilution, so we have, in reality, PV $=$ RT $-$ A, if we adopt the same form of function as that already applied with success to sulphuric acid in water. That is, the observed value of PV is lowered if we apply the correction for the heat of dilution; in other words, the true osmotic work is greater than it appears to be if the heat of dilution is neglected.   This means that our observed molecular weights are too high in the ratio of RT : RT $-$ A.   However, in the case of alcohol and benzene, the value

$$(-A) = \left(\frac{-\delta Q}{\delta x} x \right)$$

is so great that for most concentrations we obtain very large negative corrections, in most cases so large that the resulting "corrected" molecular weight is absurdly low, or even negative, as shown in Table VIII.   These values are calculated from our results at $10°$ C, the values for $\delta Q / \delta x_{10°}$ being found graphically except for the two highest dilutions, for which they were calculated by differentiation of the equation given in Table IV.   Although, as will be seen, the slope is relatively small at these dilutions the correction is so considerable that even in these cases the resulting corrected values are much lower than the observed, which are here close to the true value.   The data are given in Table VIII showing the molecular weights at different dilutions as observed by Beck-

mann, corrected as discussed in the preceding section of this paper for the change in the heat of fusion of a solvent in the presence of a solution when there is a heat of dilution.

VIII. Effect of Temperature

We have already discussed in general the form of the equation when Q varies with the temperature. If we apply this correction adopting the same form of function, we obtain still more improbable results than those given in Table VIII; the correction causes an increase in the observed molecular weight, which is already too high.

As we have shown earlier in this paper, at any fixed concentration, we have:

<div align="center">TABLE VIII</div>

Application of Heat of Dilution to Observed Molecular Weights of Alcohol in Benzene, assuming Q Independent of T

$N/n = x$	Mol. weights observed (Beckmann) Revised (Tab. VII, Col. 11)	T	RT	$\frac{\delta Q}{\delta x} 10^\circ$	$\frac{\delta Q}{\delta x} 10^\circ X$	"Mol. wt." corrected
1	2	3	4	5	6	7
1.82	308	273.5	547	—179	—326	132
2.61	256	264.5	549	—153	—400	69.5
4.02	207	275	550	—124	—498	19.3
6.66	158	275.8	551.6	—89.6	—596	—19.3
10.11	131	276.3	552.6	—67.2	—679	—30.1
16.92	100	276.8	553.6	—43.5	—736	—32.9
25.8	84.5	277.1	554.2	—30	—774	—33.5
54.2	62.9	277.6	555.2	—13.2	—716	—20.8
119.5	54.6	278	556	—3.1	—370	18.3
359	47.5	278.3	556.6	—0.49	—176	32.4

$$PV = Q_H + T \frac{d(PV)}{dT} \qquad (1)$$

Let us assume that the same solution applies as in the case of sodium in mercury, and sulphuric acid in water; also that the heat of dilution varies with the absolute temperature and is expressed by the following relation:

$$Q_H = \pm A \pm BT, \qquad (2)$$

as before, choosing our signs with the understanding that Q_H is positive if heat is evolved on dilution. A and B are constants and T the absolute temperature. By integration of (1) we obtain

$$PV = RT \pm A \pm BT \log T \qquad (3)$$

To inquire into the meaning and value of the constants A and B, we make use of the rule already discussed in which we saw that the temperature coefficient of the heat of dilution is equal to the difference in heat capacity of the liquids before and after mixing. This is discussed by Nernst[1] and Ewan;[2] the latter's expression for this, changing symbols and concentration basis to harmonize with our present requirements is:

$$Q_T = Q_{T_1} + [(m_S + m_l x)C_l - (m_S C_S + m_l x C_W)][T_1 - T] \quad (4),$$

where Q_T = molecular heat of dilution at absolute temperature T at which osmotic pressure is to be determined; Q_{T_1} = molecular heat of dilution at absolute temperature T_1, at which heat of dilution is measured. m_S = molecular weight of solute; m_l = molecular weight of solvent, as gas; C_l = specific heat of solution resulting from mixing; C_S = specific heat of solute; C_W = specific heat of solvent; $x = \dfrac{N}{n}$ = gram molecules of solvent per gram molecule of solute.

Since in (2) we are interested in $Q_H = \dfrac{dQ}{dx} x$, we differentiate Q_T with respect to x, and multiply by x:

$$\frac{\delta Q_T}{\delta x} x = \frac{\delta Q_{T_1}}{\delta x} x + [(m_S + m_l x)\frac{\delta C_l}{\delta x} + m_l C_l - m_l C_W][T_1 - T]x \quad (5)$$

In order to obtain this in the form of $\pm A \pm BT$, we have only to simplify the above:

$$\frac{\delta Q_T}{\delta x} x = \frac{\delta Q_{T_1}}{\delta x} x + DT_1 x - DTx \qquad (6)$$

where

$$D = [(m_S + m_l x)\frac{\delta C_l}{\delta x} + m_l(C_l - C_W)].$$

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[1] Theoretical Chemistry, 6th Ed., pp. 9, 161.
[2] Zeit. phys. Chem., **14**, 409 (1894).

In the case of alcohol and benzene where we have heat absorbed, Q_T is negative, likewise $\dfrac{\delta Q_T}{\delta x}\, x$.

Where $T_1 > T$ and the heat capacity after mixing is greater than before, as occurs with alcohol and benzene, the entire second member of (4) is positive in value.

Ordinarily, Q_T will, therefore, be numerically less than the heat of dilution at the temperature where this value is measured, but it will be of the same sign, namely, minus. Since, however, we assume for lack of better information, that D is always positive, where T is sufficiently lower than T_1, the second member of (6) may be so much larger than the other two members of the right hand side of this equation which are in this case of opposite sign to that of the second member that $\dfrac{\delta Q_T}{\delta x}\, x$ will be positive. This, however, is not likely to be met with in the experiment since we are ordinarily limited in our values for T by the freezing point of benzene solutions. The same considerations hold on differentiation.

We now have (6) the heat of dilution expressed as a function of the absolute temperature and in the form

$$Q_H = \pm A \pm BT \text{ — that is} \qquad (2)$$

$$Q_H = \pm \frac{\delta Q_T}{\delta x}\, x = \pm \frac{\delta Q_{T_1}}{\delta x}\, x + DT_1 x - DT x.$$

At any fixed concentration,

$$\pm \frac{\delta Q_{T_1}}{\delta x} + DT_1$$

is a constant, which we shall call A_1, to distinguish from the constant A used previously when the heat of dilution was independent of the temperature. Likewise D is a constant which to harmonize with (2) we shall call B.

From this we have

$$Q_H = \pm \frac{\delta Q_T}{\delta x}\, x = \pm \frac{\delta Q_{T_1}}{\delta x}\, x + DT_1 x - DT x = \pm A_1 \pm DT. \ (7)$$

Before going any further and substituting in the integrated

expression (3), for clearness the nature of the signs can still further be fixed for ordinary conditions. In the case of alcohol and benzene ordinarily $T_1 > T$ and $\frac{\delta Q_T}{\delta x} x$ and $\frac{\delta Q_{T_1}}{\delta x} x$ are negative, and D is positive. Therefore, in this particular case the express on assumes the form

$$Q_H = -\frac{\delta Q_T}{\delta x} x = \left(-\frac{\delta Q_{T_1}}{\delta x} x + DT_1 x\right) - DTx \qquad (8)$$
$$= A_1 - BT,$$

where

$$A_1 = -\frac{\delta Q_{T_1}}{\delta x} x + DT_1 x$$
$$B = Dx.$$

As we have already seen, if

$$Q_H = \pm A_1 \pm BT, \qquad (2)$$

adopting our original solution, we have

$$PV = RT \pm A_1 \pm BT \log T. \qquad (3)$$

Substituting (8) the expression $Q_H = A_1 - BT$ which fits this particular case, we have

$$PV = RT + A_1 + BT \log T, \qquad (9)$$

where, as before,

$$A_1 = -\frac{\delta Q_{T_1}}{\delta x} + DT_1 x$$
$$B = Dx$$

or

$$PV = RT - \frac{\delta Q_{T_1}}{\delta x} x + DT_1 x + DTx. \qquad (10)$$

If we try to apply this expression to correct the observed molecular weights of alcohol in benzene, we get a still more absurd result, namely, the correction raises the molecular weight since $DT_1 x$ and DTx are both positive and being much greater than $\frac{\delta Q_{T_1}}{\delta x} x$ will ordinarily increase rather than diminish the numerical value of the right hand s'de of the equation (10), indicating that the observed osmotic work is greater than the true value or that the observed molecular

weight is lower than the true molecular weight. As we have already seen, the observed molecular weights are already much larger than would be expected, so it seems evident that the form of function used in previous cases cannot be used here, and the correction for the heat of dilution cannot be satisfactorily applied to the observed molecular weights of alcohol in benzene.

There seems to be no question but that the observed molecular weight is always too high when heat is absorbed on dilution, and always too low when heat is evolved on dilution. Consequently a correction must be applied; but the mathematical theory of the subject has not been developed to such a point that we know how to apply the correction. If we take the simple hypothetical case in which the heat of dilution is negative and independent of the temperature the formula $PV = RT - A$ should apply to the case. If we make the further assumption that $A > RT$ we come out with an absurd result. Until this hypothetical case has been treated satisfactorily, it is hardly worth while to do more experiments. The first question to be decided is whether the error is in the original equation

$$PV = Q \pm T \frac{d(PV)}{dT}$$

or whether it is in the particular solution $PV = RT - A$.

In conclusion I wish to express my hearty thanks to Professor W. D. Bancroft for the suggestions and encouragement which he has given me in this work.

NEW BOOKS

Light and Shade and Their Applications. *By M Luckiesh. 23 x 17 cm; pp. xii + 265 New York: D Van Nostrand Co., 1916. Price: $2.50 net.—* Though this book is léss definite and consequently less interesting than the companion volume on "Color and Its Applications" (20, 539), it is a valuable book containing many exceptionally interesting paragraphs. The first six chapters are entitled· introduction; the characteristics of objects; the shadow; tne cast shadow; the scale of values; the influence of color The remaining eight chapters deal with light and shade in nature, sculpture, architecture, painting, stage-craft, photography, vision, and lighting.

In the chapter on the influence of color, we read, p 70 "A series of papers of fairly pure or saturated colors was illuminated by daylight entering a window and the reflection coefficients were determined. The same procedure was carried out when the colored papers were illuminated by the light from a tungsten lamp operating at 7-9 lumens per watt A considerable difference in the relative brightnesses (values) under the two illuminants is to be noted. It is seen that the reflection coefficient of the white surface is constant, but that this is not true of any of the colored surfaces. In general the colored papers reflecting predominantly the longer light-waves (red, orange and yellow) were brighter under the tungsten light than under the daylight Those which reflect the shorter light-waves (green, blue and violet) predominantly were brighter under the daylight than under the light from the tungsten lamp. The changes in brightness are greatest for those colors reflecting light predominantly near the ends of the spectrum "

"The foregoing effects are of importance in the use of color. For instance, a painting having an area of blue sky adjacent to yellow clouds was examined under daylight and tungsten light The clouds and sky were of equal brightness (value) when they were illuminated by tungsten light, but under daylight the sky was twice as bright as the clouds—a considerable change in relative values. Taking into account, besides this change in values accompanying a change in the illuminant the shift in hues, it is seen that the proper illuminant for paintings (and many other colored objects) is either natural or artificial daylight, because the paintings are almost always executed under natural light.

"In a study of light and shade, colored shadows should receive attention, because they are visible to the close observer almost everywhere. They are especially visible out of doors in the sunlight. Even at midday on a sunny day a shadow on a white surface is decidedly bluish in color as compared with the color of a portion of the white surface receiving light from both the sun and the sky. This is due to the bluish color of the skylight which illluminates the shadows. This effect may be observed tnroughout Nature and is quite striking in some colored objects. For instance, some green leaves appear blue-green in a shadow as compared to their green appearance in the direct sunlight. Of course the different brightnesses of objects in a shadow and in direct sunlight (the intensity of illumination from the entire sky being sometimes less than one-sixth that from the noonday sun) makes it difficult to be sure of the exact change in color. Toward evening when the sun has become quite reddish in color and the illumina-

tion due to light from the sky is approximately equal to that from the sun, the colored shadows are quite evident. Now the shadow is a vivid blue or blue-green compared with the reddish purple of the combined light from the sun and sky.

"The colored shadows are more difficult to distinguish in interiors, owing to the low brightness of the shadows, but they are often present. The colored walls and ceiling send colored light to the shadows so that the latter are distinctly colored as compared with the portion of the same surface which received considerable light direct from the light source. When the eyes are carefully screened and a white diffusing surface is used to receive both the shadow and the total light, these colored shadows are visible. A simple method of observing the effects of wall coverings in producing colored shadows is to make the observations at quite a distance from the windows which admit daylight. A striking demonstration in which the same principle is applied is to cast one shadow upon a white surface by intercepting daylight coming through a window and another by intercepting artificial light from a source in the room. The two shadows will not only be colored but will be of different color, illustrating the difference in the color of the two illuminants. In this case one shadow received only daylight and appears bluish by contrast with the other shadow, which is yellow because it is illuminated only by artificial light. The surrounding surface receives light from both illuminants, and the resultant hue is that due to the mixture of the two illuminants."

On p. 131 the author says:

"In general, low relief is seen to best advantage under lighting so highly directed that many objects molded in true proportions would appear very harsh and entirely too bold. In fact the most striking lighting effects on low relief that have come under the author's observation have been due to the direct light of the sun or of a bare artificial light source. Nevertheless much decorative relief is subjected to highly diffused light from many sources with unsatisfactory results, owing to the tendency toward obliteration. For instance, where relief is employed on ceilings and walls in interiors it would be almost invisible under the highly distributed artificial lighting systems if it were not for the superficial coatings applied, as well as the dust that collects in the interstices. When a tinted superficial coating is applied there is a tendency for thick layers to gather in the interstices, with the result that a darker tint is produced in them and hence the shadow is preserved to some extent. This, and the dust that naturally gathers in the hollows, tends to neutralize the obliterating effect of light coming from many directions. This is largely a problem for the architect."

In the chapter on architecture some of the new principles are set forth clearly, p. 168. "The most stupendous application of artificial lighting to exteriors ever attempted is found in the lighting of the Panama-Pacific Exposition. Hundreds of individual effects were obtained by lighting groups of sculpture, and whole building exteriors were often only a portion of a grand scheme. A noteworthy characteristic of this gigantic installation of lighting was the co-operation of the architects and engineers with the lighting specialists, the chief of whom was W. D. A. Ryan. The story of this wonderful undertaking and an analysis of the harmonious effects of light, shade, and color conceived with daring and executed with perfection, would fill a volume. The lighting at the Pan-

American Exposition marked the exit of the old and misconceived idea of revealing the architectural beauty at night by outlining the buildings with incandescent electric lamps where the buildings furnished a background for thousands of glaring points of light. Many of the outlined patterns were beautiful and the whole effect was spectacular; but the architectural beauty was really obscured. The lighting of the Panama-Pacific Exposition marks another epoch in the art and science of illumination. It was done chiefly by masked lighting diffused upon softly illuminated façades and emphasized by brightly lighted towers, individually illuminated sculptures, and many color effects No brief description can do adequate justice to this wonderful spectacle of light or pay due respect to the lighting genius in whose imagination it was born and through whose ability it was brought to a successful realization. The beauty of the whole exposition exterior was preserved and perhaps enhanced by concentrated effort in applying modern knowledge of the utilization of light "

The whole chapter on light and light and shade in stagecraft is both good and short, p 186. "The art of the theatre is fully realized when the text of the play, the acting, and the setting are harmoniously blended In most plays the setting should perform no more positive service than to provide a proper frame for the piece. However, the staging of the play is always of great importance and can be made to aid in the expressiveness of the text and in its appeal to the emotions and to the intellect. Light, shade, and color effects, when produced by an artist thoroughly familiar with the development of the play step by step and its aim as a whole, can not only provide a proper frame for the piece but can go further and express something that spoken words can never fully do In attempting to discuss this subject it is difficult to resist dwelling entirely upon the new movement in the theatre and to control enthusiasm for this movement which has revealed so many flaws in present stagecraft The modern theatre, of which there are very few examples in existence, is the result of the recognition of a lack of harmony of the play, its setting, and lighting The new stagecraft attempts to perfect an ideal presentation of the play

"The stage as it exists today presents many incongruous and grotesque light and shade effects. The footlights produce lighting effects that are abominable; the expression of the features of the actors is often grotesque, and the distribution of light upon the stage as a whole is unnatural. Not long ago a stage setting consisted chiefly of flat canvases upon which everything possible was painted. Now the box-set interior is common in which actual furniture is used but on the flat canvases the cornices, moldings and other projections are painted. Observation reveals the fact that these painted shadows and other light and shade effects are never in agreement with the real shadows and the distribution of light and shade produced by the stage lights. The painted perspective can never be exact, or even nearly so, excepting from only one position in the theatre. These defects have been recognized but no general attempt has been made to eliminate them. In a few theatres the footlights have been abolished and the lighting of the actors' faces has been accomplished with lights behind the proscenium arch. It is true that the footlights afford the easiest means for illuminating the actors but artificial light can so easily be controlled that the difficulties arising from the elimination of footlights can be overcome by a combination of the resources of the architect and lighting expert.

"Enclosing walls are necessary in any stage setting, but painted shadows can be reduced to a minimum and often eliminated entirely as is done in the new theatre settings. In the new theatre the few furnishings are always real instead of being merely painted with the many resulting objections, some of which have been noted in the foregoing discussion. The flats that are used should be of such surface character as to diffusely reflect the light and with the light sources properly placed a satisfactory distribution of light and shade can be obtained. With the same setting many moods can be expressed by merely manipulating the light and shade distribution on the various enclosing flat surfaces or draperies. On combining with the possibilities of light and shade those of color, the stage artist controls resources of unrealized value. · Such effects as silhouetting the actors against a bright ground or brightly illuminating the actors against a dark ground, a flood of light or a concentration of it represent extremes between which many possibilities lie. All these are obtained by the simple but artistic manipulation of lighting.

"Many of the effects obtained in the theatre are beautiful and impressive in themselves. Even the modernists of the theatre admit this but their objection lies in the lack of harmony between play and setting and the failure of many of these ingeniously arranged and lighted settings to assist the play as an 'emotional and intellectual stimulus.' The new movement was necessarily accompanied by a development of a new stagecraft. Flats, draped curtains, and folding screens of uniform tints have been used for interior and exterior walls. The few furnishings such as moldings, cornices, mantels, steps, and furniture are real, thus appearing in true perspective and casting true shadows. In the place of the back drop-curtain a sky-dome has been used in some of the European modern theatres. This consists of a dome of a translucent or diffusely reflecting medium of such a texture that the illusion of distance is obtained without unnatural perspective. This atmospheric background is natural and inconspicuous and, therefore, does not attract the attention from the action of the play. The effect is more in harmony with the aim of the play than the overdone naturalism obtained with the customary stage equipment Simplicity and the artistic use of light, shade, and color in a manner which harmonizes with the play is the keynote of the new stagecraft. There is a well marked and even unfriendly disagreement between the exponents of the old and new stagecraft, but certainly the old stagecraft will be benefited by the ideas that are being worked out in the new. Much of the discussion throughout this book is applicable to stagecraft so that it is deemed best and also sufficient to include in this chapter only a brief summary of the important features of light and shade which should receive attention in the theatre."

A few special cases of lighting are discussed on page 245. "One of the chief functions of architecture is to provide shelter and protection, and lighting can often aid in bringing forth such an impression. For instance, assume a large room crossed by beams projecting below the flat ceiling. The spaces between the beams might be either plain or ornamental. If plain, they need not be lighted very brightly, but if ornamental the illumination should be sufficient and the lighting system of such a character as to make the ornamental design plainly visible. The lighting units should not directly obscure the design as would be the case with large units hung reasonably close to the ceiling, nor

should the lighting units be much brighter than the ceiling in order to avoid obscuring the design by the glare resulting from them. Usually an indirect or semi-indirect unit would illuminate such a ceiling satisfactorily, but the height at which such units are hung is important. In this room it is assumed, as is quite usually the case, that the beams and ceiling are of high and practically equal reflecting power. In order for the beams to supply the impression of strength and stability they should be darker than the remainder of the ceiling. They can be made to appear darker either by providing their surfaces with a coating of lower reflection coefficient than the remainder of the ceiling or by illuminating them to a lower intensity. To paint them a darker shade might not always be considered possible by the decorator in his decorative plan. In such a case the lighting can be depended upon to provide the impression of supporting ability or strength. The results are quite the same in either case In order to obtain the foregoing result by means of lighting, the light sources must be hung between the beams and close enough to the ceiling so that the under side of the beams at least will receive appreciably less light than the remainder of the ceiling. This is briefly an actual condition that was difficult to solve owing to the lack of a definite correlation of architectural design, decoration, and lighting in the early plans This problem was solved by means of small semi-indirect units of low brightness hung midway between the beams and as far from the ceiling as possible without permitting direct light to illuminate the under side of the beams.

"It appears strange that the decorative possibilities of light and shade obtained by means of lighting have barely been recognized by architects and interior decorators For instance let us take the case of an actual ornamental ceiling in which one of the recurring elements of the design is a square recess of reasonable size. Such a ceiling would ordinarily be flooded with light, including the prominent beams which enclose square flat areas in the center of which, and of about one-half the total area, the recessed squares occur A so-called semi-indirect unit could be designed to illuminate the latter recesses rather brightly by means of the direct upward light, the remainder of the large square only moderately by means of light from the diffusing glass of the unit, and, if the unit were hung at a proper height, the beams would receive only scattered light Thus the supporting ability of the beams would be preserved, the decorative treatment of the ceiling would appear entirely harmonious, and general satisfaction would result from the very evident co-operation between the lighting expert, the decorator, and the architect. To obtain the foregoing result a lighting unit must be especially designed but the optical principles involved should present no difficulties to the lighting expert. Symmetry is a keynote in such designs. Why should not the lighting be accurately and designedly symmetrical? The symmetrical arrangement of the ceiling outlets is not sufficient, for it is symmetry in lighting effects and ornamental design that is often necessary to complete the harmony.

"Let us consider another case, namely a large dome with a small skylight at the top and arches intersecting the lower portion of the dome on the four sides. Obviously the lighting possibilities can be almost as varied as the general decorative treatment. A dome can be made to express the spaciousness of out-doors, the mystery of the dark sky, or the shadowless conditions of an over-

cast day, respectively, by high, low, or moderate brightness. These effects can be enhanced by a proper lighting of the intersecting archways. The whole can be considered as an interior lighted primarily by means of a patch of sky —the skylight—as in the case of the Pantheon at Rome which is lighted through a circular unglazed orifice in the crown of the dome. The entire dome might be faintly lighted from a pedestal at the center of the floor and the shadow of the dome deepened by contrast with the brightly lighted archways. Another treatment which would result in the dome proper being of relatively low brightness would be to light only the archways directly, the dome receiving only a portion of the reflected light. These treatments are simple from a lighting standpoint, but the one selected should aid in carrying out the architect's conception. It is obvious that the lighting results might very often tend to defeat the artistic expression conceived by the architect. Too often, even during the first lighting of beautiful architectural works, there is insufficient co-operation between the lighting expert, the architect, and the decorator, and this mistake is very common in the redesign of lighting systems in beautiful old buildings."

Wilder D. Bancroft

A Laboratory Guide to the Study of Qualitative Analysis. *By E. H S. Bailey and H. P. Cady. Eighth revised edition 21 × 15 cm; pp. x + 294. Philadelphia: P. Blakiston's Son and Co , 1916. Price. $1 50 net.*—In the preface the authors say: "In the revision for this edition no change has been made in the general plan of the work. Some typographical errors have been corrected, and some sections which experience has shown are difficult of comprehension by the student, or not sufficiently definite, have been amplified or rewritten. The introduction has been changed so as to include the relation of the change of the freezing point and of the boiling point of a solution to its change in vapor pressure, and here some paragraphs have been rewritten. Type equations to explain the experiments performed have been included in the case of a few more complicated reactions. The order of arrangement has also been changed somewhat by placing both the systems for the separation and identification of the ions after all the preliminary experiments to both of anions and of cations, in order that it might more conveniently be preceded by the general directions for analysis of unknown substances. It is not the intention that the student shall complete the entire list of preliminary experiments before any analyses are made."

The fact that eight editions have appeared speaks well for the book.

Wilder D. Bancroft

La Chimie des Eléments Radioactifs. *By Frederick Soddy. Translated by E. Philippi. 22 × 14 cm; pp. 175. Paris: Gauthier-Villars and Cie, 1915. Price: 5 francs.*—This is a translation of the English edition which appeared in 1915 and which already has been reviewed at length (**19,** 339). It is a pleasure to see that the war has not destroyed the market for this excellent book.

Wilder D. Bancroft

THE DENSITY OF SILICON TETRAFLUORIDE

BY ALBERT F. O. GERMANN AND HAROLD S. BOOTH

Among the gases whose physical constants have been little studied, the fluoride gases are perhaps pre-eminent. The reason for this seems to be the indication by most experimenters that these gases slowly attack glass at room temperature,[1] giving rise to various by-products which would vitiate results; furthermore, the purification of these gases presents an unusually difficult problem. In recent years, however, the opinion has gained ground that many reactions will not proceed in the absence of traces of moisture. So, for example, perfectly dry nitric oxide gas, as well as nitrogen peroxide, when left in contact with dry mercury at room temperature, leaves the surface of the mercury unattacked; the merest trace of moisture, however, suffices to tarnish the surface. We decided, therefore, that the action of the fluoride gases on glass might depend upon the presence of traces of moisture.

Preliminary work on the subject, using silicon tetrafluoride as the experimental gas, both on account of the ease with which it may be prepared and because of its high fluorine content, demonstrated the fact that at least this fluoride, when perfectly dry, attacked neither glass nor mercury, even after five months of contact.

With this assurance, we decided to undertake the accurate determination of the weight of the normal liter of silicon tetrafluoride, and eventually of other physical constants of the gas, as the opportunity offered. This determination seemed all the more important because all but one of the published values were made before the modern technique in the measurement of gas densities had been developed. And it is evident that any effort to arrive at a satisfactory value for the atomic weight of fluorine by physico-chemical methods must end in failure until modern methods are applied.

[1] See, for example, H. Rose: Pogg. Ann., **80**, 406 (1850).

Historical

There have been very few determinations of the density of silicon tetrafluoride. Four of these are of historical interest only. The earliest is that of J. Davy,[1] who found its specific gravity, compared to air, to be 3.5735. In 1827 Dumas[2] found a value of 3.6. Dalton found a value compared to air of 4.17, which is apparently much too high. Truchot,[3] in 1884, following the method of Chancel,[4] found for the value of the density of silicon tetrafluoride compared to air, 3.6. These determinations were made by crude methods, no adequate means having been used to purify the gas or to avoid the absence of air or of hydrogen fluoride.

There is only one modern determination of the density of silicon tetrafluoride, that of Jaquerod and Tourpaian,[5] in 1913. These authors used the principle of Archimedes, that of a light glass globe floating in the gas whose density is to be determined, and checked their results by the globe method. They found the value

$$L_N \text{ (silicon tetrafluoride)} = 4.693 \text{ g,}$$

a value which according to the same authors[6] gives for the atomic weight of fluorine, 19.09, which is unquestionably too high. The gas used was probably purer than any used before for a density determination, since, in addition to the usual precautions for its preparation, the gas was condensed and purified by fractional sublimation. A list of these values is given in Table I. A careful search of the literature has failed to reveal any others.

TABLE I

J. Davy	1812	3.5735 (air = 1)
Dumas	1827	3.6 "
Dalton	—	4.17 "
Truchot	1884	3.6 "
Jaquerod and Tourpaian	1913	L_N = 4.693

[1] Phil. Trans., **102**, 352 (1812).

[2] Ann. Chim. Phys., (2) **33**, 370 (1826); Pogg. Ann., **9**, 418 (1827).

[3] Comptes rendus, **98**, 821 (1884).

[4] Ibid., **94**, 626 (1882).

[5] Jour. Chim. phys., **11**, 3 (1913).

[6] Ibid., **11**, 269 (1913).

Preliminary Work

Our first efforts were directed toward determining whether silicon tetrafluoride attacked glass. For this purpose we set up a generator and prepared the gas, passing it through a drying tube, D_1 (Fig. 3), consisting of alternate sections of glass wool and phosphorus pentoxide to remove hydrogen fluoride and the water resulting from its reaction with the glass wool. Then we solidified this gas with the aid of liquid air. We let it stand in contact with the mercury of the manometer M_1 over night and found no action on the glass or on the mercury in the morning; and this in spite of the fact that the silicon tetrafluoride had escaped by way of the manometer during the night. Thus encouraged we decided to make a preliminary determination of the density, using the apparatus shown in Fig. 3 with the exception that pressure manometers M_2 and M_3 were only safety manometers of a capacity of from a vacuum to atmospheric pressure. We tried to purify the gas by distilling from the solidified silicon tetrafluoride in one distilling tube to the other tube, rejecting the first and last fractions; in fact, the method used by Jaquerod and Tourpaian. We repeated this distillation, or rather sublimation, five times, hoping to obtain a pure gas. We observed during the sublimation that the current of gas from the surface of the solid carried along particles of a solid gas which soon volatilized when removed from the neighborhood of the solidified silicon tetrafluoride; this we had every reason to believe was an impurity. We endeavored to avoid this by slowing down the rate of distillation but were not successful. Using the gas which we had attempted to purify in this manner, we made a determination of the density. The value thus found for the density was too low and we were therefore forced to the conclusion that this method of sublimation was not a satisfactory method of purification for silicon tetrafluoride.

It is a well known fact that the most satisfactory method of purifying a gas, aside from the chemical methods, is the fractional distillation of the liquefied gas.[1] Moissan[2] in-

[1] See Germann. Jour. Phys. Chem., **19**, 451 (1915).
[2] Comptes rendus, **139**, 711 (1904).

dicates that solid silicon tetrafluoride changes to a liquid
under a pressure of two atmospheres and a temperature of
—77° C.   Our next step was to modify the apparatus so as to
be able to carry out the purification by distilling the liquefied
gas.   The simplest method at hand was to construct a pressure
device such as that shown in Fig. 3.   Here the wide tubes
A have a volume three times that of the narrow tubes B
per unit length, and tubes B are three times as high as tubes
A, so that, when pressure forces the mercury in the wide tube
to a point near the bottom, the mercury rises three times as
far in tube B, thus enabling us to work with a range of pres-
sures from a vacuum to several atmospheres.

Method

The globe method essentially as described in detail by
Germann[1] was chosen for its rapidity and accuracy and was
carefully followed out with the exception that three globes
and only one barometer were used.

This method in our present state of knowledge eliminates
practically all sources of error or reduces them to a minimum.
For example, the use of several flasks eliminates gross errors
in calibration and in weighing, and the possibility of error
due to condensation of the gas upon the inner surface of the
globe when the gas is admitted is materially reduced by using
flasks of different sizes.

Description of the Apparatus

The apparatus used was of course constructed entirely
of glass.   In no place was any rubber tubing or foreign sub-
stance allowed to come in contact with the silicon tetrafluoride
except in the stopcocks and at the ground flat joints J by which
the globes were attached to the apparatus.   Here a special
rubber-vaseline grease was used which our experience shows
is practically unaffected by silicon tetrafluoride.   The stop-
cocks on the apparatus were all of the capillary variety,
especially made for vacuum work.

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[1] Jour. Phys. Chem., **19**, 437 (1915).

The barometer used was the type described by Germann[1] with a glass scale made by the Société Genevoise pour la Construction des Instruments de Physique. The barometer was carefully cleaned by filling with chromic acid and allowing it to stand over night. It was then rinsed and filled with strong nitric acid containing a few drops of alcohol and allowed to stand for several hours and then washed with distilled water. It was then placed in position, and air, dried by sulphuric acid and phosphorus pentoxide, was passed through the apparatus continuously for one week to remove all adsorbed moisture. After being allowed to stand evacuated for several days, it was filled with mercury without heating. This mercury was purified by first agitating with 10% nitric acid by means of a suction pump, next passing through a mercury tower containing the same reagent, and finally distilled in a vacuum in an all-glass apparatus.

The temperature of the room was so constant and the time of reading was so short that it was found unnecessary to surround the barometer with an air bath. Three carefully calibrated thermometers were mounted beside the glass scale, one near the upper mercury surface, one near the center and one at the bottom. The barometer was read with the aid of a cathetometer, an electric light immersed in a bath of water arranged on a pulley behind the barometer case providing illumination. The corrected barometer reading was obtained by applying the temperature[2] and gravity[3] corrections. The residual pressures in the globes were measured with a modified McLeod vacuometer which had a ratio of one actual millimeter to 19.16 mm as read on the scale. Vacuum was obtained by a water suction pump and the mercury pump. The globes in which the gas was weighed were round bottom flasks selected from the stock of distilling flasks; these were drawn out at the neck and glass stopcocks with

[1] Jour. Am. Chem. Soc., **36**, 2456 (1914).
[2] Landolt-Börnstein, page 18 (1912).
[3] See page 86.
[4] Germann and Cardoso: Jour. Chim. phys., **10**, 406 (1912).

flat joints sealed on (see J in Fig. 3). Flasks from the same stock were chosen corresponding in air displacement to the density globes and filled with distilled water until they weighed two grams more than the corresponding glass-cocked flask. They were then sealed off in a crook to be used as counterpoises. The density globes were calibrated according to the method outlined by Germann.[1] This method is simply evacuating and weighing, filling the globes with air-free distilled water at zero and weighing, and then emptying, evacuating and weighing. The difference between the weight filled and the average of the weights evacuated was the weight of water contained at the temperature of melting ice.

To find the volume at zero, the following corrections had to be applied:

1. Correction for the buoyancy of the air on the weights used. The average weight of a cubic centimeter of air in Cleveland is 0.00117 g, and therefore the correction amounted to $\frac{W}{8.5}$ × 0.00117, where W is the weight of water and 8.5 is the density of brass; the correction is negative.

2. Correction for volume of water at zero; if the density of water at zero is taken as 0.999868, the correction is W × 0.000132 and is positive.

3. Correction for latitude and altitude. The value of the gravity constant at Cleveland may be theoretically determined by substitution in the following formula:

$$G_0 = \frac{1 + \dfrac{2h}{R}}{1 - \delta \cos 2\phi}$$

where h is the altitude above sea level which at the well of our barometer was 219.5 meters, where R is the average radius of the earth, 6367382 meters, and where ϕ is the latitude at the point of observation, here, $41°30'15''$, and where δ is a constant which is given as 0.0025935 by Lasch.[2]

[1] Jour. Phys. Chem., **19,** 459 (1915).

[2] Pogg. Ann. Erg., **3,** 321 (1853).

Substituting these values in this equation we get the value of 1.0003847. The ratio of the gravity constant at sea level, g_n, to the gravity constant, g_m, as determined experimentally in our physics laboratory, is

$$G_o = \frac{g_n}{g_m} = \frac{980.616}{980.240} = 1.0003835$$

Theoretical Value = 1.0003847
Experimental Value = 1.0003835

With a difference of only   0.0000012

The values were averaged and rounded off to $G_o = 1.000384$, which is the most probable value of the gravity constant at the Morley Laboratory.

The algebraic sum, Σ, of these corrections becomes Σ = 0.000384 W + 0.000132 W — 0.000138 W; therefore W + 0.000378 W = true volume of globes.

The following table gives the results of several concordant measurements on each globe:

TABLE II

	Volume	Correction	Corrected volume
Globe E	332.487 g water	0.126	332.61 cc Booth
Globe F	573.435 g water	0.216	573 65 cc Booth
Globe D	203.658 g water	0.077	203.765 cc Germann
Globe A	631.17 g water	0.238	631.41 cc Germann

An important source of systematic error that was neglected until Rayleigh called attention to it in 1888[1] is the contraction of the globe when it is evacuated, causing it to displace less air than before and hence apparently to weigh more. To correct this error it is necessary to find the amount of the contraction. Fig. 1 shows the globe enclosed in a stout inverted bell jar supplied with a flat plate glass top which could be clamped on tightly by thumb screws. This flat plate had an inch hole provided with a one-holed rubber stopper slit so as to permit putting it on the neck of the flask.

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[1] Proc. Roy. Soc., **43**, 361–2 (1888); Chem. News, **57**, 74 (1888).

The calibrated capillary tube was fitted into the lid by grinding it into place in a hole through the plate. The bell jar was filled with water, the rim greased with rubber-grease and the flat plate clamped on so that the water stood at some point in the capillary; the globe was evacuated; the level of the water in the capillary tube noted; then air was allowed to fill the globe rapidly and the level of the water again noted. The volume of the capillary between the two points noted was the amount of contraction of the globe. The average of several determinations was taken as the final value. Results are included in Table III.
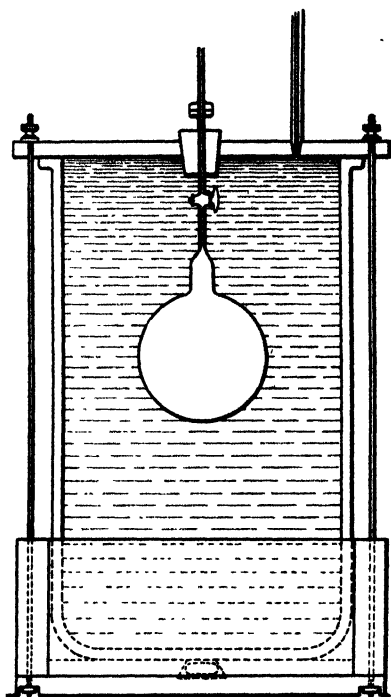
The weights used in this work were gold plated brass weights, supplied by the Scientific Materials Co. and were carefully calibrated against a standard ten gram weight (Reichsanstalt) according to the Kohlrausch method.

Fig. 1

TABLE III

	Gross weight of flask	Contraction cc	Air displaced per liter
Globe D	65 grams	0.008 cc	0.000047 g Germann
Globe E	113 grams	0.0232 cc	0.00008 g Booth
Globe F	139 grams	0.0495 cc	0.00010 g Booth
Globe A	113 grams	0.040 cc	0.000074 g Germann

An ordinary chemical balance was employed. To increase the accuracy the pans were removed and light aluminium

trays were suspended close under the knife edges by means of fine platinum wire. These trays were designed to receive the weights and leave the lower part of the balance case free to receive the globes and their counterpoises. The balance case itself was surrounded by a much larger glass case with doors opening from the front. Across the top of this outer case was stretched a nickel wire from which the globes with their counterpoises were hung preparatory to weighing.

For the preparation and purification of the silicon tetrafluoride used, special forms of apparatus were e m p l o y e d. The generator G (see Figs. 2 and 3) was made of a large thick-walled round-bottomed distilling flask, the neck of which bore two tubes, the delivery tube D and tube H for admitting the sulphuric acid. The reservoir R containing the conc. sulphuric acid was made of a large calcium chloride tube. To control the amount of sulphuric acid being admitted to the flask, a needle valve, consisting of a large glass stirring rod, S, ground in place in the small end of the tube and held in place at the top, was used.
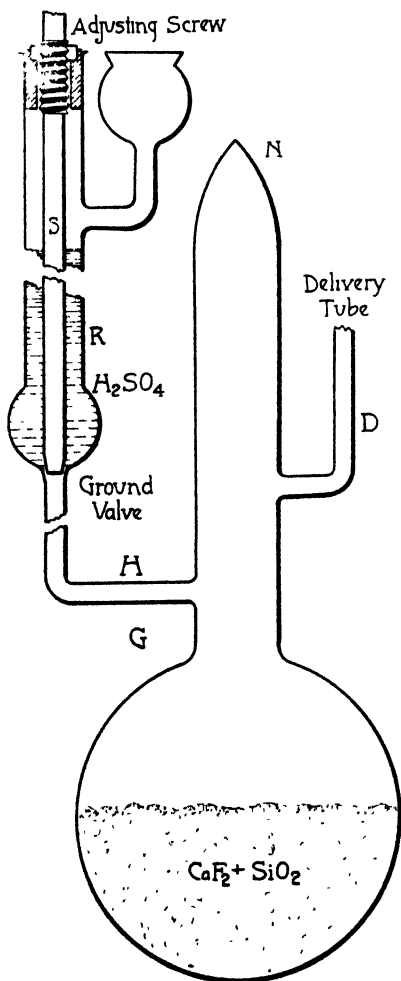

Fig. 2

The adjustment was controlled by means of a threaded collar slipped over this rod and held in place by sealing wax; this threaded collar engaged threads of a brass nut fastened on a cork which fitted snugly in the

upper end. When the needle valve was turned down into place, there was no difficulty in getting a perfect vacuum in
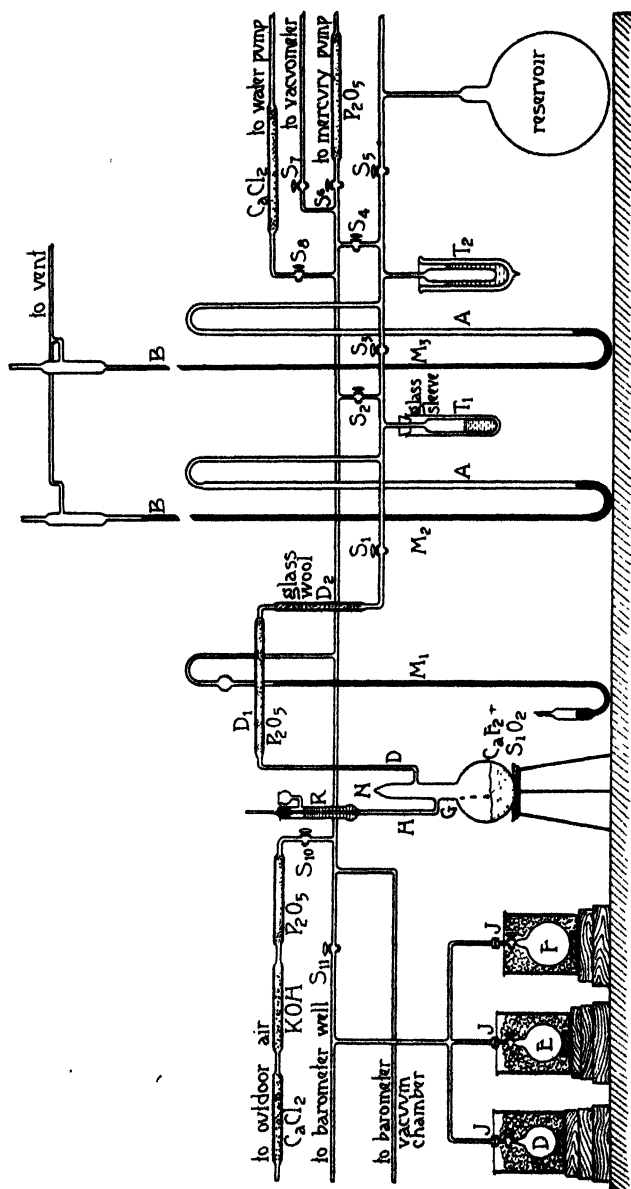

Fig. 3

the flask.[1] No heat was applied in generating gas, the sand bath being used merely as a support for the flask, and for safety in case of accident.

The gas generated in the flask passed from the delivery tube through a drying tube, D_1, containing seven alternate plugs of glass wool and phosphorus pentoxide and then through tube D_2 containing glass wool. In the first tube the plugs of glass wool reacted with any hydrofluoric acid generated, forming silicon tetrafluoride, the water from this reaction being absorbed by the phosphorus pentoxide. No action was observed in this tube farther than the third plug.

From this point the gas passed into the apparatus designed for purification by physical methods. Through the stopcock S_1 gas entered directly into the liquefaction bulbs T_1 and T_2 separated by stopcock S_3, each supplied with a manometer, M_2 and M_3.

In distilling from one bulb to the other, a glass sleeve was placed around the bulb from which the gas was distilling in order to prevent superheating. To the distilling apparatus a reservoir of about fifteen or twenty liters capacity was connected through stopcock S_5. Each distilling bulb was also connected through a stopcock, S_2 and S_4, to a main line to which was connected by means of stopcocks a mercury pump, vacuometer, water suction pump and a safety manometer, M_1. To this main line, through a series of drying and absorption tubes carbon-dioxide-free and water-free air could be admitted through stopcock S_{10}. Through stopcock S_{11} gas was admitted to the globes and to the well of the barometer. During distillation stopcocks S_1, S_2, S_3, S_4 and S_5 were provided with brass clamps to withstand the pressure.

Manipulation

Before beginning the measurements the globes were clamped in position and the entire apparatus was evacuated and

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[1] Both these pieces of apparatus and the apparatus used for the determination of the contraction of the globes were home-made affairs, but answered their respective purposes as well as the imported apparatus.

allowed to stand over night in contact with the phosphorus pentoxide tube of the mercury pump.

Generation of Gas

The flask G was half filled with a well ground mixture of one part calcium fluoride and two parts pure sea sand. Broken pieces of soda glass were scattered over the surface of this mixture to insure a large excess of silica. Then the neck of the flask was drawn out and sealed off at N (Figs. 2 and 3). Sulphuric acid was placed in the reservoir R and the ground valve opened enough to wet it and then reseated tightly. The generating flask was evacuated and left to stand over night in contact with phosphorus pentoxide in D_1 (Fig. 3). The large reservoir was similarly evacuated as completely as possible and the whole system was left in contact with the phosphorus pentoxide of the mercury pump through S_6. Next morning sulphuric acid was allowed to drip slowly upon the mixture in the generator, and the gas evolved condensed in T_1 by surrounding it with liquid air in a Dewar flask, as at T_2.

When a sufficient quantity of the solid silicon tetra-fluoride had been condensed the supply of acid was shut off and when generation ceased, stopcock S_1 was closed.

Distillation and Purification

All stopcocks communicating with the distilling tubes were then clamped. The liquid air was changed to surround T_2, while T_1 was wiped with alcohol and the glass sleeve slipped over it. (Fig. 3 shows this arrangement.) The pressure in T_1 was allowed to increase until nearly all the silicon tetrafluoride was liquefied. The fractionation of the liquid followed. The first and last fractions—no less than 200 or 300 cubic centimeters of gas in each case—were allowed to escape by opening stopcock S_2 and pumping off with the water pump. The middle fraction was condensed in T_2. At least five such distillations were made before the gas was considered to be pure. During the last two distillations the

gas distilled at a constant pressure and the purified liquid was perfectly limpid and colorless.

In the distillation of liquefied gases a criterion of the purity of the gas is given by the pressure exerted during the distillation. The pressure remains constant as long as the composition of the distillate does not change and the distillation proceeds quietly.

Stopcock S_5 was finally gradually opened and the silicon tetrafluoride distilled into the reservoir.

The difficulty attending the handling of silicon tetrafluoride is the constant necessity for watchfulness against the presence of water vapor. To make sure that the apparatus was perfectly dry, the whole system before filling was left evacuated in contact with phosphorus pentoxide. The next day the apparatus, including the density globes, was rinsed three times with air, free from moisture and carbon dioxide, admitting the air through stopcock S_{10} and pumping it out by means of the water and mercury pumps. Then the rinsing was continued using silicon tetrafluoride admitted from the large reservoir, until it was deemed that the apparatus was free from air. In this case, the evacuation was facilitated by the use of liquid air, condensing all the gas used for rinsing purposes in one of the condensing tubes, and evacuating from this reduced volume; it is evident that any non-condensable gases would be dragged into the condensing tube, along with the silicon tetrafluoride. The residual pressure of silicon tetrafluoride, by means of the vacuometer, and the temperature, were noted. The stopcocks of the globes and all stopcocks except S_{11} were then closed. The connecting tubing was then rinsed several times with dry air admitted slowly through S_{10}. Stopcocks S_{10} and S_{11} were then closed and the globes removed. The rubber-grease was washed from the flat joints with ether and the globes and counterpoises were washed with distilled water and wiped dry with a clean cloth and then wiped bright with a piece of good quality of white silk which left no lint. The globes and counterpoises were suspended in the outer balance case and weighed the next

morning. The weighings were carried out exactly as described by one of us.[1] Globes D and E were allowed to swing on the knife edges ten minutes, Globes F and A, fifteen. Three sets of weighings were made and the average of the three weighings taken.

This represented the weight that had to be added to the globe plus the small weight of silicon tetrafluoride it contained at a pressure of p millimeters, to cause equilibrium to be established with the counterpoise. It was necessary to correct, then, for the small amount of silicon tetrafluoride still in the globe; if V be the volume of the globe expressed in cc, p the pressure in millimeters read on the vacuometer, and T the absolute temperature of the gas when the reading was made, the amount of the correction is given by the expression

$$\frac{4.684 \times 273 \times V \times p}{1000 \times 760 \times T} = \frac{0.001682 V p}{T}.$$

This correction is positive and must be added to the weight found.

The globes were then transferred to the laboratory, where they were placed in position, and the pressure in each measured to be certain that no air had entered in the interval, care having been taken to evacuate and rinse with air and then silicon tetrafluoride several times the space between the stopcocks of the globes and S_{11}.

The afternoon was devoted to the fractionation of silicon tetrafluoride from the large reservoir and filling the globes with it. A sufficient quantity for filling the globes was condensed in tube T_2 and refractionated as already described. The first and last fractions, no less than 200 or 300 cc of gas in each case, were pumped off. The middle fraction was condensed in the second liquefaction tube. At least three such distillations were made before the gas was considered to be pure. Stopcocks connecting to the globes were then opened. By lowering the Dewar flask surrounding the distilling tube containing the liquid silicon tetrafluoride, the liquid gas was allowed to distil slowly into the globes. When the pressure

[1] Jour. Phys. Chem., **19**, 466 (1915).

of the gaseous silicon tetrafluoride in the globes neared 760 mm, the barometer was placed in communication with the apparatus and distillation stopped when the pressure was approximately 762 mm.[1] Two pressure readings were made on the barometer with the aid of the cathetometer and the average of the readings taken. The thermometers accompanying the barometer were read as the pressure readings were made. The globe stopcocks were closed and then those leading to the barometer.

After the silicon tetrafluoride in the rest of the apparatus had been recondensed in the distilling tube, the system was thoroughly rinsed with dry air. This ended the operation of filling. The globes were removed from the ice, carefully washed, wiped dry and placed in the weighing case as before to remain over night. Three weighings were made the next day. The averages of these weighings were the weights of the globes filled with silicon tetrafluoride at the pressure P read on the barometer.

On the afternoon after the weighing, the globes were evacuated by condensing the gas in tube T_1 and allowing the gas to distil into the reservoir. This gas was thus constantly being used and purified by fractionation. The globes were then weighed exactly as already described. The averages of the corrected weights of the globes evacuated before and after filling were considered the real values of the weights of the evacuated globes. Then the difference between the weight of the filled globe and that of the empty globe gave the weight of the gas it contained at zero degrees centigrade and H mm pressure. The calculation of the gross weight of the liter followed by the application of this formula:

$$L_{gross} = \frac{760W}{HV}$$

Where W is the weight of the gas found and L_{gross} the uncorrected weight of the liter of gas. The corrections to be applied were as follows:

[1] Application of barometer correction brought this value back to about 760 mm.

1. A positive correction for the contraction of the globes during evacuation. Since this contraction involves an apparent increase in the weight of the globe when it is evacuated, due to the smaller volume of air displaced by it, the value of the correction C_c is evidently given by the additional weight of air that would be displaced if the globes were not evacuated. This weight on the basis of a liter, assuming the average weight of a cubic centimeter of air in Cleveland to be 0.00117 g, and expressing the amount of the contraction in cubic centimeters by C, is given by

$$C_c = \frac{1000 \times 0.00117 \times C}{V} = \frac{1.17\,C}{V}.$$

Substituting the values for the contraction found for the globes used in this formula, we obtained the positive corrections set down in Table III.

2. Correction for the buoyancy of air on the weights. Since only those weights come into consideration that are used to replace the silicon tetrafluoride when the globes are empty, the gross weights employed may be neglected and the calculation made on the basis of a liter, 4.684 g. The weight of air displaced, R_v, using as the density of brass 8.5 and assuming that all weights were made of brass[1] is given by

$$R_v = \frac{4.684 \times 0.00117}{8.5} = 0.0006445 \text{ g}$$

a negative correction.

3. Positive correction for the altitude or reduction to sea level and $45°$ N latitude. This correction, G (see page 86 this article) is made as follows:

$$G = L_{gross}\,(1.000384 - 1.00) = 4.684 \times 0.000384 = 0.00180$$

4. Correction for the compressibility of silicon tetrafluoride. This correction was very small because the pressure at which the globes were closed before weighing, was always as nearly as possible equal to 760 mm, the average of the pressures used being 760.41 mm. The value of the coefficient of compressibility for silicon tetrafluoride derived from critical data is, according to Jaquerod and Tourpaian,[2]

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[1] See Gray and Burt: Jour. Chem. Soc., **95**, 1636 (1909).

[2] Jour. Chim. phys., **11**, 3 (1913).

$$A'_0 = 0.005244$$

$$\text{and } A = 0.00524 \times \frac{760 - 760.41}{760} \quad L = -0.00013 \text{ g.}$$

Applying these corrections to the gross weight of the liter of gas we have the expression

$$L_N = L_{gross} + C_r - R_v + G + A.$$

In practice the correction for the contraction of the globes during evacuation, C_t, was applied to the individual results, since the correction varied from globe to globe; the other corrections were applied to the average obtained.

Results

The results obtained for the density of silicon tetra-fluoride purified by fractional distillation under pressure as described are tabulated in Table IV. Globe F was broken when being taken from the ice in the second measurement and thereafter Globe A took its place. The barometric readings in the third column are the corrected readings. The gross weight in the fourth column is the weight of the silicon tetrafluoride contained in the globe at the time of measurement corrected for the inaccuracies of the weights. The value L_{gross} is obtained by application of Boyle's law, while in the next column the weight of the gross liter has been corrected for the contraction of the globes (see Table III).

TABLE IV

Measurement	Globe	Corrected barometer mm	Gross weight g	L_{gross} g	$L_{gross} + C_t$ g
I	D	761 42	0.93755	4 59255	4 59260
I	E	761.42	1.53064	4.59332	4.59340
I	F	761 42	2.63884	4 59213	4.59223
II	D	759.76	0.94401	4.63430	4.63435
II	E	759.76	1.54031	4.63244	4.63252
III	D	761.52	0 95586	4.68162	4.68167
III	E	761.52	1.56036	4.68189	4.68197
III	A	761.52	2.96280	4.68285	4.68292
IV	D	759.30	0.95343	4.68338	4.68343
IV	E	759.30	1.55745	4.68682	4.68690
IV	A	759.30	2 95274	4.68075	4.68082

It will be remembered that we were continually re-using and purifying the same gas by fractionally distilling and storing in the reservoir. It is apparent in Table IV, which records the results of all measurements made by us, that the density was progressively rising (corresponding to greater purity) until the third set of measurements. In sets III and IV the results were concordant. This was considered an index to the absolute purity of the gas.[1] Although at each fractionation the liquefied gas seemed perfectly limpid and colorless, yet we cannot consider that fact a sufficient criterion and have used only sets III and IV in the calculation of the final result.

The average of the values of the last two sets of measurements is $L_{gross} + C_c = 4.68295$. The weight of the normal liter becomes, using the values already found for R_v, G and A:

$$L_N = (L_{gross} + C_c) - R_v + G + A = 4.68397 \text{ g}$$

Discussion of Results

As has been mentioned, the only value for the density of silicon tetrafluoride which may be classed as modern that to our knowledge has been published up to the present time, is that of Jaquerod and Tourpaian,[2] who found

$$L_N = 4.693 \text{ g.}$$

This value differs from the value found in this research by two parts in one thousand, a difference which is too great to be attributed merely to experimental error. The methods used in both researches are standard methods, which have been used successfully by the same experimenters on other gases.[3]

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[1] It is also possible that equilibrium had not been established between the glass of the globes and the gas.

[2] Loc. cit.

[3] See the authors: Western Reserve University Bulletin, Vol. 19, No. 8, page 45 (1916), on "The Density of Air in Cleveland;" here the same apparatus was used, and the value found for air,

$$L_N \text{ air} = 1.29273 \text{ g}$$

coincides with the average of results of other investigators. Also A. F. O. Germann, "The Density of Oxygen," Jour. Phys. Chem., 19, 437 (1915); and "The

Hence it would seem that the error must be found in another direction. The purity of the gas employed may next be considered. We have already pointed out that the gas we used was used over and over, being subjected to renewed purification after each set of measurements. The results show that by this procedure some impurity, lighter than the gas in question, was progressively eliminated, until in the third set of measurements the purification seems to have been complete, inasmuch as no further change in density was found. It may be recalled at this point too, that our first efforts at purification, by distillation under diminished pressure, were entirely fruitless so far as the preparation of a pure gas is concerned, the values so found having all been too low. In the preparation of the gas, it will be recalled, we used no heat, but allowed the reaction to go on at room temperature, the heat of reaction being rather low, and in the presence of a large excess of finely divided silica and of glass wool. This was amply sufficient to arrest all hydrogen fluoride, as at the end of the measurements no part of the apparatus showed even the slightest etching. Jaquerod and Tourpaian, on the other hand, carried out the preparation of the gas by heating the reacting materials, and subsequently passing the gas over glass wool at 100° C. The preliminary work of these authors brought out the fact that when the gas was passed over red hot glass wool, the results were too high, which caused them to suspect the formation of a sesquifluoride of silicon.[1] Hence their adoption of the lower temperature to remove hydrogen fluoride. They, however, gave no evidence which would indicate that the formation of sesquifluoride did not take place

Density of Air in Geneva," Jour. Chim. phys., **12**, 103 (1914), who found the following values by the globe method:

$$L_N \text{ oxygen } = 1.42905 \text{ g}$$
$$L_N \text{ air } = 1.2930 \text{ g}$$

Jaquerod and Tourpaian: Arch. Sci. phys. nat., (4) **31**, 20 (1911), who found, applying the principle of Archimedes,

$$L_N \text{ oxygen } = 1.4290 \text{ g}.$$

[1] Troost and Hautefeuille: Ann. Chim. Phys., (5) **7**, 464 (1876).

at 100° C.   Assuming the formula of the sesquifluoride to be Si_4F_6, by analogy with silicon sesquichloride, a simple calculation will show that only 0.16 percent by weight of this impurity would suffice to raise the density of silicon tetrafluoride by two parts in one thousand.   Moreover, the method of fractional distillation used by Jaquerod and Tourpaian is, to say the least, unsatisfactory, inasmuch as the distillation, or rather sublimation, proceeds only on the surface of the solid, where less volatile impurities, having once collected on the surface, may easily be carried along by the current of volatilizing gas—a circumstance, besides, which was actually observed in the course of our preliminary experiments.   This is, of course, entirely prevented by the liquefaction of the gas by the application of pressure.

The theoretical value of the density of the normal liter of silicon tetrafluoride, considering the molecular weignt to be 104.3, is lower than either of the values discussed above.[1]   Our value, 4.68397 g, differs from it, therefore, much less than the value found by Jaquerod and Tourpaian.   As the fifth decimal place has little significance, this may be rounded off to 4.6840 g.

Conclusion

Considering the care taken in purifying the gas used in these measurements, and the precautions taken generally throughout this series of measurements, we believe that the value for the density of silicon tetrafluoride found above more nearly expresses the true density of the gas than any yet published.   We therefore propose as the weight of the normal liter of silicon tetrafluoride,

$$L_N = 4.6840 \text{ g.}$$

In conclusion, we wish to express our gratitude to the Linde Air Products Co., of Cleveland, who supplied the liquid air for this research, and but for whose coöperation this work could not have been carried out.

The Morley Chemical Laboratory
Western Reserve University
Cleveland, Ohio

[1] A study of this subject will be undertaken in a separate paper.

MOLECULAR ATTRACTION. XIII. RELATIVE TO AN ARTICLE BY A. P. MATHEWS[1]

BY J. E. MILLS

It is always with regret that I publish an article only to discuss the work of another. But a recent article by A. P. Mathews contains so much of value that the article will receive attention, and I therefore feel compelled to point out the very erroneous ideas that he advances in explaining my own equation and the equation of Dieterici.

First.—It is obvious that two equations which are simultaneous and true can be combined, and the resulting combined equation will also be true. Consequently the several equations that I have from time to time derived, and several others that I have investigated, have been combined with other equations in various ways. But I have consistently refused to combine these equations with the equation of van der Waals,

$$\text{I.} \qquad \left(P + \frac{a}{v^2}\right)(V - b) = R\,T,$$

because that equation, as is well known, is not correct.

In the above equation a/v^2 is the term added in order to allow for an effect produced by the cohesive or molecular forces, and is usually termed internal pressure.

I have calculated and published an expression for the internal pressure derived theoretically upon the assumption of an inverse square law of force, and have accumulated considerable evidence to show that my expression is correct.

Now Mathews, in a round about way, as will be shown later, simply substitutes my (I think correct) expression for the internal pressure for van der Waals' incorrect expression, and thereby is enabled to calculate "a" of van der Waals' equation correctly at the critical temperature. He is pleased with the result (of that I am glad) and, by one of those oversights which it is so difficult to avoid, thinks that this proves the

[1] Jour. Phys. Chem., **20,** 554 (1916).

efficiency of van der Waals' equation and furnishes an explanation of my own work on molecular attraction. As a matter of fact the substitution proves nothing at all except that the *substituted expression was correct* if the results obtained are correct. Since the substituted expression was my own, I at least am glad if correct results were obtained. The correctness or incorrectness of the original equation of van der Waals cannot of course be determined by such a substitution, and some of Mathews' admiration of that equation for the results he obtained ought in reason to have been distributed elsewhere.

Mathews makes exactly the same mistake with regard to an equation derived by Dieterici and investigated and extended by myself and others.

Needless to say, had Mathews reached his conclusions directly he would not have fallen into the errors he made. Probably he overlooked an article[1] by the author on internal pressure. In that article, page 263, Equation 10, there is given for the internal pressure p in millimeters of mercury the expression,

$$2. \qquad p = \frac{31414\,\mu'}{3V^{4/3}},$$

where V is the volume of one gram in cubic centimeters. (So far as the critical temperature is concerned the calculation had been published several years before.)

If we let a/v^2 of van der Waals equal this expression at the critical temperature, we have, since V of van der Waals' equation is the volume of a gram molecular weight,

$$3. \qquad \frac{a}{M^2 V_c^2} = \frac{31414\,\mu'}{3V_c^{4/3}}, \text{ or } a = \frac{31414\,\mu'\,V_c^{2/3}M^2}{3}.$$

Changing from volume to density, and from pressure in millimeters of mercury to calories we have the equation in the form given by Mathews as his Equation 26,

$$4. \qquad a = \frac{\mu'\,M^2}{3d_c^{2/3}}.$$

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[1] Jour. Phys. Chem., **19,** 257 (1915).

If "a" is calculated according to this equation and sub-stituted in van der Waals' equation the operation is of course identically the same operation as rubbing a/v^2 out of van der Waals' equation and writing in its place the value given in Equation 2. Yet from this operation Mathews claims to have discovered an explanation of my equation, calculating μ' of my equation in terms of "a" and failing entirely to realize that the operation he performed was the substitution of my equation for the internal pressure for van der Waals' expression in toto. Nor was any attempt made to show that "a" thus calculated at the critical temperature was a constant at other temperatures or volumes.

As regards Dieterici's equation I also showed in the paper cited,[1] page 269, Equation 17, that the internal pressure could be expressed as,

$$5. \qquad p = \frac{CRT}{V},$$

an equation probably exactly true only at the critical tem-perature. Mathews similarly substitutes this expression for van der Waals' a/v^2 and finds in consequence also an "ex-planation" of Dieterici's equation. See Mathews' Equations 14 and 15.

$$6. \qquad \frac{a}{M^2V_c{}^2} = \frac{CRT_c}{V_c}, \text{ or } a = CRT_cV_c.$$

Had Mathews taken a third expression for the internal pressure at the critical temperature given in the paper above cited, namely,

$$7. \qquad p = \frac{dP}{dT}\,T_c - P_c,$$

he could in an exactly similar manner have derived a most interesting "explanation" of the Clausius-Clapeyron thermo-dynamical equation. Then finding the mine so rich he would undoubtedly have suspected that it was salted.

Second.—Mathews compares the "a" calculated by Equation 4 with the "a" calculated by Equation 6. Of course

[1] Jour. Phys. Chem., **19,** 257 (1915).

in comparing two functions one can multiply or divide them by any desired quantity but such multiplication adds nothing new to a comparison, and the relation between μ' and C for 30 substances is shown in Table 2, page 1120.[1] Also the equation

$$8. \qquad \frac{dP}{dT} = \frac{2R}{V_c}$$

and the values of μ' calculated by its aid are there shown. *Mathews' Tables III and IV add absolutely nothing new.*

Third.—The fact that

$$9.\ C = \frac{\mu'^{\,3}\sqrt{d_c}}{3RT_c} = \frac{\text{energy necessary to overcome molecular attraction}}{2 \times \text{kinetic energy of molecules}}$$

was pointed out by the author in 1909.[2] Compare this with Mathews' statement at the bottom of page 575.

Fourth.—Mathews, in Equation 38, page 591, and Table VI, gives the relation between the internal and the external critical pressures also as something new brought to light by his discussion. This Equation 38 is the same as my Equation 21[3] with the term "S" transposed from one side of the Equation to the other.

Fifth.—Mathews refers to Dieterici's equation for the internal heat of vaporization as being theoretically grounded and says that my own expression is an empirically discovered relation. I have already tried to convince Mathews[4] that my equation was theoretically derived. *It was entirely so derived. No experimental evidence whatever was examined until the equation was complete.* Dieterici, on the other hand, has this to say[5] concerning his relation: "Die Beziehung,

$$10. \qquad \lambda = CRT \ln \frac{V}{v},$$

ist als richtig zu betrachten; das Resultat ist ohne jede

[1] Jour. Am. Chem. Soc., **31**, 1099 (1909).

[2] Ibid., **31**, 1117 (1909).

[3] Jour. Phys. Chem., **19**, 655 (1915).

[4] Ibid.; **18**, 104 (1914).

[5] Drude's Ann., **25**, 574 (1908).

hypothetische Annahme allein durch Berechnung gewonnen, die sich unmittelbar auf das Beobachtungsmaterial stützt; ist also als ein reines Beobachtungsergebnis zu betrachten."

Sixth.—On page 567 Mathews calculates the energy required to get one molecule into the surface layer and then multiplies this value by the number of molecules to get the total energy required. This procedure is contradictory to the law of force he gives on page 589. If his argument on page 567 is correct the force must vary as the mass and not as the square of the mass. The same mistake is repeated on pages 568 and 570. (Mathematically in my own work, insofar as the mass is concerned, I can proceed as Mathews does on page 567, since the law of attraction that I have found to be true does require the force to be proportional to the mass and not to the square of the mass.) I make the above criticism humbly as I fell into identically the same error in my first paper.

Seventh.— On page 563 Mathews says, "since only the vertical component of the molecular motions tends to carry the molecules from the liquid to the vapor, the increase will be proportional to the cube root of the temperature interval from the critical." See also page 571. If V' is the velocity in any direction and x is the vertical component, it is usually supposed that $\dfrac{V'^2}{3} = x^2$.

In investigating the work of Goldhammer and Eötvös and in attempting to find a simple relation between gravitational, molecular, and chemical forces, Mathews' work is of real value. While I do not agree perhaps with all of his arguments, I particularly hope that his work in the latter direction will prove of real significance and I do not see why the errors pointed out in this article should affect the real value of that work.

Summary

It is shown that Mathews in his recent discussions of equations by Dieterici, Mills, and van der Waals, simply substitutes for the internal pressure term in the last equation

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the more correct expressions previously derived and published
by the author from the first two equations. Consequently
his conclusions as regards these three equations are wrong.
Other mistakes are mentioned. The essential part of his
work on the relations of Goldhammer and Eötvös and on the
attractive forces is not vitiated by these mistakes."

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        Oct. 14, 1916

THE PASSIVE STATE OF METALS

BY C. W. BENNETT AND W. S. BURNHAM

The phenomenon of passivity was probably first noted with iron,[1] when treated with concentrated nitric acid. The general property has later been found marked in the cases of aluminum, chromium, nickel, tin, and cobalt. Passivity[2] is also found in the cases of tungsten, molybdenum, silver, bismuth, platinum, zinc, magnesium, copper, lead, columbium, vanadium, niobium, ruthenium, gold, tantalum, uranium, manganese, and to some extent probably with most of the metals under extreme conditions. Attempted explanations of the facts of passivity have dealt largely with iron, consequently in this discussion iron will be studied more in detail than other cases of passivity. The other metals will be considered however.

The passive state of iron is a condition, which it acquires when it is exposed to the action of oxidizing agents, whereby its surface becomes more noble, in other words its solubility is decreased. The single potential is a noble one, rather than the less noble one associated with iron itself. The measurement of this potential has been used to test the presence of the passive state.[3] It has led to many contradictions, however, on account of the fact that different solutions are used and different values obtained. Furthermore, too much depends on the method of measurement. The non-replace-

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[1] Keir: Phil. Trans. (orig.), **80**, 359 (1790); Abridged by Hutton, Shaw and Pearson (1809), **16**, 694 (1785-1790).

[2] See Dunstan and Hill: Jour. Chem. Soc., **99**, 1853 (1911).

[3] Keir: Loc. cit.; Wetzlar: Schweigger's Jour., **56**, 206 (1829); Fechner: Ibid , **53**, 61, 129, 151 (1828); Joule: Phil. Mag., (3) **24**, 106 (1844); Beetz: Pogg. Ann., **67**, 286, 365 (1846); Corsepius: Beiblätter, **11**, 272 (1887); Dissertation, Munich (1886); Martens: Mém. de l'Acad. de Bruxelles, **19**, 3 (1845); Hittorf: Zeit. phys. Chem., **34**, 385 (1900); Michell: Arch. Sci. phys. et nat., (4) **10**, 122 (1900); Finkelstein: Zeit. phys. Chem., **39**, 91 (1902); Fredenhagen: Ibid., **43**, 1 (1903); Muthmann and Frauenberger: Sitzungber. kgl. bayr Akad., **34**, 210 (1904).

ment of copper or silver ions has also been used.[1]   The use
of nitric acid of such strength that passive iron when placed
therein remains passive but in which active iron dissolves
readily,[2] is the most satisfactory criterion of passivity.   For
the sake of uniformity, since there are degrees of passivity,
we may take Heathcote's test for the passive state of iron.[3]
He employed nitric acid, testing the chemical action.   "The
rod was regarded as passive when after plunging in 1.2 nitric
acid, and shaking for a moment in the acid and then holding
motionless, no chemical action could be detected at the surface
by the unaided eye, the temperature of the acid being about
15°–17° C."   The nitric acid referred to above is 1.20 specific
gravity.

    A number of investigations have been made on passive
iron, and the reaction has been considered from a number of
viewpoints.   Keir[4] noted that only strong nitric acid rendered
iron passive, and that when passive iron was scratched, or
brought in contact with active metal, it become active.

    These experiments seem to have been lost sight of and
the facts were rediscovered by Wetzlar.[5]   The position of

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[1] Wetzlar· Schweigger's Jour., **49,** 470 (1827), Fischer: Pogg. Ann., **6,**
42 (1826); Wöhler Ibid , **85,** 448 (1852); Senderens: Bull. Soc. chim., Paris,
15, 691 (1896); **17,** 279 (1897), de Brenneville· Jour. Iron and Steel Inst., **52,**
40 (1897).

[2] Herschel. Ann. Chim. Phys., (2) **54,** 87 (1833); Schönbein: Pogg.
Ann , **37,** 390, 590 (1836); Mousson: Ibid., **39,** 330 (1836), Bibl. univ de Genève
(Sept., p. 165 (1836)), Faraday: Phil. Mag., (3) **9,** 53, 122 (1836); Noad: Ibid.,
(3) **10,** 276 (1837); (3) **12,** 48 (1838); Herschel· Ibid., (3) **11,** 329 (1837); Rénard:
Comptes rendus, **79,** 159, 508 (1874), de Regnon: Ibid., **79,** 299 (1874); Varenne:
Ibid., **89,** 783 (1879); **90,** 998 (1880); Nichols· Am. Jour. Sci., (3) **31,** 272 (1886);
Nichols and Franklin: Ibid., (3) **34,** 419 (1889); Belck: Dissertation, Halle,
a. s. (1888); Gautier and Charpy· Comptes rendus, **112,** 1451 (1891); Andrews:
Proc. Roy. Soc., **49,** 120 (1891).

[3] Heathcote: Jour. Soc. Chem. Ind , **26,** 899 (1907). I should state
here that the freest use has been made of the excellent bibliography in this article,
as well as that in Byers' paper noted below.

[4] Phil. Trans., Loc. cit   Bergman it seems also noted that iron did not
dissolve in silver nitrate solution.   Phil. Trans. (orig.), **80,** 374 (1790).   Abridged
by H., S., and P. (1809), **16,** 703 (1785–1790).

[5] Wetzlar. Schweigger's Jour., **49,** 470 (1827); **50,** 88, 129 (1827); **54,**
324 (1828); **56,** 206 (1829); **58,** 302 (1830).   See also Broconnot: Ann. Chim.
Phys., (2) **52,** 288 (1833); Pogg. Ann., **29,** 174 (1833).

passive iron in the electrochemical series was determined by Fechner.[1]

Westlar[2] attributed the inability of iron to replace copper after being placed in silver nitrate, to the assumption of a negative charge by the part immersed.

Herschel[3] published the first results explaining passivity on the basis of electrical phenomena. Publishing in 1833, the results of his work in 1825, he says that "passive [*prépaié*] iron may be withdrawn from the acid and exposed to the air, dipped in water or ammonia without regaining acitivity [*la propriété d'être attaquée par l'acide nitrique*]. It may be touched lightly in the acid or in the air with gold, silver, platinum, mercury, glass, and many other substances without destroying the passive state. But if the surface be rubbed vigorously, giving intimate contact, for instance; if it is scratched with the edge of a piece of glass, the passive state is destroyed   On the other hand, if passive iron in water, air, or in the acid, be touched with copper, zinc, tin, bismuth, antimony, lead, or active iron, passivity is destroyed   . If a long iron wire passivated and moistened with acid is touched with copper at one end, while suspended in air, the surface becomes brown, not instantaneously, and all at once, but by a progressive [*successivement*] movement, spreading, so to speak, from the end touched to the other   Once passivified, iron resists nitric acid of the concentration in which it was passivated, or even more dilute, which shows that these phenomena are due, not to a lack of solvent for the iron salt, but rather to a certain *permanent electrical condition of the surface* of the metal. This viewpoint is strengthened by following experiments. . .

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[1] Fechner: Schweigger's Jour., **53**, 129 (1828); see also Ibid., **53**, 151 (1826); Pogg. Ann , **47**, 1 (1839).

[2] Ann. des Mines (Third Series), **2**, 322 (1832); *Mag. Pharm., 1830.* The references printed in italics have not been checked. These publications were not readily available. The above Westlar is probably the same as Wetzlar, the former being a French misspelling of the German "Wetzlar." This however could not be determined with certainty, because the original paper of Westlar (sic) was not available.

[3] Herschel: Ann. Chim. Phys., (2) **54**, 87 (1833); Pogg. Ann., **32**, 211 (1834); Phil. Mag., (3) **11**, 329 (1837).

"A piece of iron wire was coated with wax in the center, so that the piece was divided into two parts. When this wire was put into strong nitric acid, action stopped on each end at the same time; when one end was touched with copper, action started simultaneously on each end ... [*when however*] the iron was withdrawn from the acid into the air, and then touched, the action started at the end touched and ran the whole half of the wire, but was stopped by the wax." In this condition, if the wire is dipped into the dilute acid, the whole was observed to become active, although the experiment was performed in a little different way.

Schönbein who suggested the term passivity next studied the subject.[1] He found that when a part of an iron rod was passivated, by dipping deeper into the dilute acid a larger surface could be passivated. If two pieces of iron, one active and the other passive were partly immersed in dilute nitric acid, and then electrically connected outside of the acid, the active rod becomes passive if the immersed surface is not too great. If the surface is much greater than the immersed area of the passive rod, the latter will become active. The combination becomes passive or active depending on the relative areas of the original active and passive rods. It was also found that iron could be passivated when made anode in nitric acid, and that the passive state was destroyed by touching the iron with the negative electrode. With the source of current used, the circuit had to be closed by putting the iron in the acid, otherwise passivity was not produced. When there was set free at the iron surface any substance like chlorine which has a "strong affinity" for iron, no passivity could be produced. Iron was, therefore, made passive when anode in nitric acid, sulphuric and phosphoric acids, but could not be made passive under these conditions when chlorides, bromides, fluorides, or iodides were used.

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[1] Schönbein: Phil. Mag., (3) **9**, 53, 259 (1836); (3) **10**, 133, 172, 267, 425, 428 (1837); (3) **11**, 544 (1837); Pogg. Ann., **37**, 390, 590 (1836); **38**, 444, 492 (1836); **39**, 137, 342, 351 (1836); **40**, 193, 621 (1837); **41**, 41, 55 (1837); **43**, 1, 13, 89, 103 (1838); **57**, 63 (1842); **59**, 149, 421 (1843); *Bibl. univ. nouv Serie*, **9, 416; 18, 366;** *Arch. de l'Électr.*, **2, 269 (1842).**

He concluded that bismuth[1] could be passivated, but cobalt and nickel could not.

Faraday[2] in answer to a request of Schönbein to explain his results noted that active iron in 1.25 acid was made passive by touching with gold, platinum, or carbon. Oxide films, which are invisible to the naked eye, and also insoluble in nitric acid, are formed by heating iron in air or oxygen. Since such a protection of the metal is possible, and on account of the fact that all passivifying processes are oxidation processes, Faraday concluded, that "the surface of the iron is oxidized, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte, as to be equivalent to an oxidation. .

"The state seems to me to be one of a very delicate equilibrium of forces, though of course that condition of things which can produce it can also retain it; and this notion seems to be confirmed by the intermitting action originally mentioned by Herschel."

Nickles[3] showed that nickel and cobalt may also be passive. Nichols and Franklin[4] showed that passive iron dissolves slowly in nitric acid. Buff[5] showed that aluminum was passive under a variety of conditions. Beetz[6] reviewed and tested previous work but developed very little otherwise. This is also true of the large volume of the literature published from the time of Faraday's and Schönbein's work,[7] until Hittorf revived interest in passivity by his work on chromium.

[1] See Andrews: Phil. Mag., (3) 12, 305 (1838); Pogg. Ann., 45, 121 (1838); Proc. Roy. Soc. (London), 46, 176 (1889); 48, 116 (1890); 49, 481 (1891); Nature, 43, 358 (1891); Beiblätter, 14, 1144 (1890); 15, 428 (1891).

[2] *Faraday: Experimental Researches, 8th Series, sec. 947–996 and Vol. 2, 237;* Phil. Mag., (3) 9, 53, 122 (1836); (3) 10, 175 (1837).

[3] Nickles: Comptes rendus, 37, 284 (1853); Pogg. Ann., 90, 351 (1853).

[4] Nichols and Franklin: Loc. cit.

[5] Liebig's Ann., 102, 265 (1857).

[6] Beetz: Pogg. Ann., 62, 234 (1884); 63, 415 (1844); 67, 186, 365 (1846); *Arch. de l'Électr., 4, 509, 600; Rep. der Physik, 8, 256 (1859);* Pogg. Ann., 127, 45 (1866); Wied. Ann., 2, 94 (1877); *Münch Ber., 1875, 59;* Pogg. Ann , 156, 464 (1875).

[7] This list taken from the several reviews of the subject referred to below contains references not heretofore given down to the work of Hittorf on chromium

A number of solutions besides nitric acid may develop the passive state of iron without the aid of an external current. Keir passivified iron with a solution of silver nitrate; Kirwan used lead nitrate; Boutmy and Chateau,[1] potassium perman-

(1898). *Kirwan: "On Phlogiston," Precipitation of Metals, p. 244 (1789);* Vanquelin: Scherer's Allg. Jour. Chem., *3, 331 (1799),* Thenard: Ann. Chim., 56, 59 (1805); Sylvester: Gehlen's Jour. Chem. Phys., 1, 539 (1806); Davy: Gilbert's Ann., 51, 206 (1815); Phil. Trans., 116, Pts. 2–3, 383 (1826); Ann. Chim. Phys., (2) 33, 276 (1826); Pfaff: Gilbert's Ann., 69, 84 (1821); Schweigger's Jour., 53, 77 (1828); Oersted: Ann. Chim. Phys., (1) 22, 358 (1823); Avogadro: Ibid., (1) 22, 361 (1823); Marianini: Schweigger's Jour., 49, 452 (1827); Ann. Chim. Phys., (2) 45, 40 (1830); De la Rive: Ibid., (2) 36, 34 (1827); Pogg. Ann., 10, 425 (1827); *Arch. de l'Électr., No. 5, 267;* Schweigger and Siedel: Schweigger's Jour., 53, 167 (1828); Van Beek: Pogg. Ann., 12, 274 (1828); Berzelius: Jahrbuch, 8, 104 (1829); Daniell: Phil. Trans., 126, 114 (1836); *Wartmann: Essai historique sur les phénomènes de l'electrochimie (1838);* Maas: Bull. Acad. roy. de Bruxelles, 6, 2nd Pt., 438 (1839); *Chateau and Boutmy: Cosmos, 19, 117;* Grove: Phil. Mag., (3) 15, 292 (1839); Pogg. Ann., 48, 300 (1839); 49, 600 (1840); 63, 424 (1844); *Arch. de l'Électr., 4, 167;* Martens: Pogg. Ann., 55, 437, 612 (1842); 61, 121 (1844); 63, 412 (1844); Bull. Acad. roy. de Bruxelles, 7, 1st Pt., 393 (1840); Millon: Pogg. Ann., 57, 289 (1842); Comptes rendus, 21, 47 (1845); Ohm: Pogg. Ann., 63, 389 (1844); Phillips: Phil. Mag., (3) 33, 509 (1848); Wöhler: Pogg. Ann., 85, 148 (1852); Liebig's Ann., 82, 248 (1852); Wheatstone: Phil. Mag., (4) 10, 143 (1855); *Heerer: Mitt. Gewerbver: Hannover, 342 (1855);* Osann: Pogg. Ann., 96, 498 (1855); Wöhler and Buff. Liebig's Ann., 103, 218 (1857); Kestner: Ann. Chim. Phys., (3) 55, 330 (1859); Anon.: Jour. prakt. Chem., 83, 209 (1861); Heldt: Ibid., 90, 257–288 (1863); St. Edmé: Comptes rendus, 51, 507 (1860); 52, 930 (1861); 106, 1079 (1888); 109, 304 (1889); *Peretti: (Pamphlet) Dell' Azione chimica dell' Acqua sopra i Soli e sopra gli Acidi, Rome (1861);* Ordway: Silliman's Am. Jour. Sci., (2) 40, 316 (1865); Jour. prakt. Chem., 99, 366 (1866); Tomlinson: Proc. Roy. Soc. (London), 16, 403 (1868); 17, 240 (1869); 18, 533 (1870); Phil. Mag., (4) 34, 136, 229 (1867); Jour. Chem. Soc., 22, 125 (1869); Cailletet: Comptes rendus, 68, 395 (1869); Ducretet: Jour. Phys., 4, 84 (1875); Comptes rendus, 80, 280 (1875); Moissan: Ibid., 84, 1296 (1877); 86, 600 (1878); Ramann: Ber. Deutsch. chem. Ges., 14, 1430 (1881); Bibart: Nature, 24, 179 (1881); Oberbeck: Wied. Ann., 19, 625 (1883); Laurie: Phil. Mag., (5) 22, 213 (1886); Streintz: Wied. Ann., 32, 116 (1887); 34, 751 (1888); Veley: Proc. Roy. Soc., 46, 216 (1889); 48, 458 (1890); Jour. Chem. Soc., 60, 525 (1891); Neumann: Zeit. phys. Chem., 14, 193 (1894); Ditte: Comptes rendus, 110, 573 (1890); 128, 195 (1899); Ann. Chim. Phys., (7) 16, 152 (1898); Pollak: Comptes rendus, 124, 1443 (1897); Gratz: Wied. Ann., 62, 323 (1897); Askenasy: Zeit. Elektrochemie, 4, 70 (1897); Lecher: Sitzungsber. Akad. Wiss., Wien, 107, 2a, 739 (1898); Guthe: Phys. Rev., 15, 327 (1902); Bredig and Haber: Ber. Deutsch. chem. Ges., 31, 2741 (1898); Scott: Wied. Ann., 67, 388 (1899).

    [1] *Cosmos, 19, 117.*

ganate and dichromate, chloric acid, and arsenic acid; Schön-
bein, mercuric nitrate and sulphuric acid to which nitrous
acid is added; Wetzlar, copper potassium tartrate and am-
moniacal copper solution; while Beetz used chromic acid.
Varenne showed that compressed nitric oxide will make iron
passive. Young and Hogg[1] have shown that iron when be-
coming passive may adsorb weighable amounts of nitrogen
peroxide, and that on exposure to moist atmosphere this comes
out with the formation of drops of acid on the piece of metal.
Boutmy and Chateau with Muthmann and Frauenberger
have shown that oxygen from the air will develop the passive
state of iron. Renard claims that the vapors of strong nitric
acid will cause passivity.

The process is not instantaneous, but a certain time is
used to develop the state. This time varies with the condi-
tions of electrolyte, temperature, etc. It is found, however,
that the time required for passivity varies inversely with the
oxidizing (in a general sense) power of the solution. If the
metal be made anode, the time required for passivity varies
inversely with the current density with the exception that at
low current densities, iron, for instance, does not go passive
at all. With an anode voltage less than 0.65[2] no passivity
occurred in sulphuric acid. As anode the metal becomes
more noble gradually until finally it reaches practically a
stationary state at about —0.75 volt (absolute), in sulphuric
acid. A sample of the metal seldom acts the same in being
passivated repeatedly.

The active condition is restored by making the metal
cathode or bringing it in contact with the cathode, by stirring

[1] Young and Hogg: Jour. Phys. Chem., **19,** 617 (1915); see also Weber:
Jour. prakt. Chem., **114,** 342 (1873).

[2] Heathcote: l. c.; for other reviews see *Schönbein: Das Verhalten des
Eisens zum Sauerstoff (1837)*; Berzelius: Lehrbuch, Vol. II, 629 (1844); Wiede-
mann: Lehrbuch der Elektricität, Vol. II, 812 (1894); Ostwald: Elektrochemie,
696 (1896); *Sackur: Chem. Ztg., 28, 954 (1904)*; Fredenhagen: Zeit. phys. Chem.,
63, 1 (1908); Byers: Jour. Am. Chem. Soc., **30,** 1718 (1908); *Grave: Jahrbuch
der Radioaktivität u. Elektronik, 8, 91 (1911); Friend: The Corrosion of Iron
and Steel, Chap. 12 (Longmans), 1911;* Senter: Trans. Faraday Soc., **9,** 203 (1914).

or scratching. Keir and Buff noted that passive iron becomes active when placed in water. Noad found that dilute nitric acid destroyed passivity. Schönbein found that either chlorine bromine, hydrochloric acid, sulphuric acid, or potassium chloride solution restored the active state. This change is just the reverse of the passivifying operation. The metal becomes less noble until finally activity is restored. Considering the voltage-time curve of either process, there is a more or less rapid rise or drop to an intermediate value where the voltage is very nearly constant with time, and then another rather sudden rise or fall of the voltage, and the metal is no longer active or passive as the case may be. Above this nearly constant voltage the metal is always passive while below this, it is always active. Martens claims that passive iron when placed in an activifying solution of copper sulphate becomes coated with a good deposit of copper, very different from that obtained by immersing iron in the copper solution. This shows probably that the activation is a process which exposes the metal surfaces only gradually. Belck and Varenne claim that passive iron becomes active when placed in a vacuum. Heathcote, however, has shown that iron may be kept passive in a vacuum for hours. Spots of activity may occur, however, and some of the samples become active under such influence.

While iron is passive it is really dissolving. Faraday showed that iron as anode in nitric acid dissolves slowly. Heathcote showed that the rate of solution is the following. The current was 0.085 ampere for 18 minutes.

Specific gravity of nitric acid	Iron dissolved Gram
1.40	0.0141
1.30	0.0108
1.15	0.0079

Without the current the indications are that the rate of solution is less the more dilute the acid, although this cannot be said with certainty since there are so many factors that

may vary. It is impossible to measure the solubility under such conditions. The phenomenon must, therefore, be considered as dynamic rather than static. In fact, Heathcote emphasizes this when he says "the appellation 'passive' is only true so far as the sense of sight is concerned; passive iron is really the seat of a multitude of changes."

This is realized when one considers the pulsation of activity and passivity mentioned by Herschel. In passivifying a piece of iron a surge or pulsatory movement of the zone of passivity back and forth very often occurs. In fact, if two strips of iron are connected to a galvanometer and dipped in a passivifying solution, there will be a pulsation of current back and forth. This may be followed on a rod by watching the evolution of gas. When passive iron is touched with a less noble metal a surge back and forth will occur. Pulsations often take place just before passive iron becomes active when placed in dilute nitric acid.

A number of the properties of passive and active iron have been studied in attempts to explain passivity. The reflecting power of the material in the two states has been measured.[1] A piece of iron was polished and made anode and cathode successively in a passivifying solution. Oxygen was deposited at the surface as anode and hydrogen at the surface as cathode. No difference in the reflecting power of the anode and cathode was noted, although the method was claimed to be sufficiently accurate to detect a film of oxide, $0.8\mu\mu$ thick in the case of lead. This caused these observers to say there could be no *oxide film* present.

Since the above experiment showed negative results in distinguishing by physical means between active and passive iron, some physical properties which show differences may be given. When aluminum is made anode in sulphuric acid, for instance, it is covered with an insoluble film of oxide which contains some gas in its pores. This covering may be considered as a di-electric where the metal and electrolyte form

[1] Müller and Königsberger: Zeit. Electrochemie, 13, 659 (1907); Phys. Zeit., 5, 413, 797 (1904); 6, 847 (1905); 7, 796 (1906); Beiblätter, 29, 711 (1905).

the two conductors. The arrangement may be considered
an electro-static condenser[1] which will show "capacity."
Passive iron in most cases shows such capacity,[2] while active
iron does not. The experimenters conclude that a solid film
must be assumed to explain their results.

When a polished metal plate is exposed to ultraviolet
light, it readily loses a negative charge, becoming positively
charged. A measure of this loss of negative charge is known
as the photo-electric effect of the metal. This has been
measured and it was found that active iron exhibits a strong
photo-electric effect, while passive iron shows much less, and
sometimes scarcely a measurable effect.[3] Metals exposed to
air show photoelectric fatigue or a decrease in the photo-
electric activity. This falls in line with the statements of
Muthmann and Frauenberger that atmospheric air may passi-
sivify iron. Just as iron may show degrees of passivity,
so does it show degrees of photo-electric activity. The
phenomena of chemical activity and photo-electric activity
of iron vary concomitantly, and have, therefore, been referred
ultimately to the same general cause.

Faraday's explanation of the passivity of iron was more
or less accepted, and Wiedemann rather without evidence
put down the oxide as Fe_3O_4, which has gradually crept into
the text-books and some of the literature on the subject.
This view was called in question when the next important
case of passivity was studied. Hittorf[4] showed that when
chromium is dipped in oxidizing solutions it becomes passive,
and is more noble than silver or mercury. It does not reduce
gold, platinum, or palladium chloride even at the boiling
temperature. Evidently the solutions were not concentrated.
The temperature probably was not much above 100° C.

[1] See Schulze: Trans. Faraday Soc., **9**, 268 (1914).

[2] Gordon and Clark: Jour. Am. Chem. Soc., **28**, 1534 (1906); Zeit. Elek-
trochemie, **12**, 769 (1906).

[3] Allen: Proc. Roy. Soc., **88**, A, 70 (1913); Trans. Faraday Soc., **9**, 247
(1914).

[4] Zeit. phys. Chem., **25**, 729 (1898); **30**, 481 (1899); Zeit. Elektrochemie,
4, 482 (1898); **6**, 6 (1899); *Sitzungsberichte Berliner Akademie, Mar. 10 (1898)*·
Zeit. phys. Chem., **34**, 385 (1900); Zeit. Elektrochemie, **7**, 168 (1900).

It was found that chromium could be passive or active in the same solution when the chromium was anode, depending on the temperature. Chromium as anode dissolves in zinc chloride solutions at ordinary temperatures as hexavalent ion and the metal is in its noble condition. In other words, it is passive. At elevated temperatures under the same conditions otherwise, the chromium is active and dissolves as bivalent metal. In the case of $ZnCl_2$, the temperature has to be 130° C. In this state chromium is less noble than hydrogen.

In an alcoholic solution of zinc chloride Hittorf claims that chromium dissolves as trivalent ion, and the metal occupies an intermediate state in the voltaic series. This has later been shown to be due to experimental error.[1] Some alcohol is oxidized to aldehyde. If this is neglected the valence may range from 2.25 to 11.9, depending on the conditions of temperature and current density. The more alcohol oxidized the higher the apparent valence of the chromium.

Active chromium replaces hydrogen and forms chromium iodide, when placed in hydriodic acid, but passive chromium is not affected by hydriodic acid or even as anode in potassium iodide. Furthermore chromium may be made to assume the passive state, when made anode in potassium iodide solution. This was considered as conclusive by Hittorf that the passivity of chromium was not due to an oxide film. He also included iron with nickel and cobalt in this class, since he showed that these metals may assume the passive state. He concludes that passivity is due to a strained or coerced condition (Zwangzustand) of the metal whereby it dissolves with different valences. There is no attempt to determine what causes the change in the metal.

Nickel in air is passive. It will not replace copper from copper sulphate. Nickel is passive as anode in sulphuric acid,[2] or sulphates, nitrates, and alkalies Byers claims prac-

[1] Kuessner: Zeit. Elektrochemie, 16, 769 (1910).
[2] Le Blanc and Levi: Boltzmann's Festschrift, 183 (1904); Riesenfeld: Zeit. Elektrochemie, 12, 621 (1906); Thiel and Windelschmidt: Ibid., 12, 737 (1906); Sackur: Ibid., 14, 607 (1908); Byers: Jour. Am. Chem. Soc., 30, 1741 (1908); Alvares: Zeit. Elektrochemie, 15, 142 (1909); Schoch and Randolph: Jour. Phys. Chem., 14, 719 (1910); Schoch: Trans. Faraday Soc., 9, 274 (1914).

tically no solution of a passive nickel anode, while Sackur claims that it dissolves slowly. The passivity is hindered by rise in temperature.

Cobalt may be made passive as anode in carbonates, bichromates, oxalates, and alkalies. In sulphates the passivity is periodic and occurs only at high current densities.

Grube[1] has shown that iron, lead, silver, and zinc become passive when made anode in alkaline solutions of potassium ferrocyanide. Anodes of iron, nickel, cobalt, copper, lead, and silver become passive in neutral solutions of potassium ferro-cyanide. He observes that passivity is accompanied by the appearance of a visible film.

Magnesium[2] will become passive anodically and under such conditions dissolves with a valence of nine.

Tin becomes passive in sodium stannate solutions[3] anodically.

The passivity of aluminum, coupled with its "valve action," has been studied closely.[4] The film which is unquestionably present is a nonconducting one, hence it is probably not continuous. A film of gas serves to give the aluminum electrode "capacity."[5] Aluminum is passive in air, and re-

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[1] Grube: Zeit. Elektrochemie, 18, 189 (1912); Trans. Faraday Soc., 9, 214 (1914).

[2] Baborovsky: Zeit. Elektrochemie, 11, 465 (1905).

[3] Eckardt: Zeit. phys. Chem., 56, 391 (1906).

[4] Buff: Liebig's Ann., 102, 265'(1857); Beetz: Wied. Ann., 2, 94 (1877); Pollak: Comptes rendus, 124, 1443 (1897); Graetz: Zeit. Elektrochemie, 4, 67 (1897); Norden: Ibid., 6, 155, 188 (1899); Ditte: Ann. Chim. Phys., (7) 16, 152 (1898); Comptes rendus, 110, 573 (1890); 128, 195 (1899); Guthe: Phys. Rev., 15, 327 (1902); Burgess and Hambeuchen: Trans. Am. Electrochem. Soc., 1, 147 (1902); König: Elektrotechn. Zeit., 23, 474 (1902); Taylor and Inglis: Phil. Mag., (6) 5, 301 (1903); Nodon: Electrochem. Ind., 1, 222, 284 (1903); Int. Elect. Cong. (St. Louis), 1, 510 (1904); Electrochemist, 3, 444, 772 (1904); Fischer: Zeit. Elektrochemie, 10, 869 (1904); Cook: Phys. Rev., 18, 23 (1904); Charters: Jour. Phys. Chem., 9, 110 (1905); Zimmerman: Trans. Am. Electrochem. Soc., 5, 147 (1904); 7, 309 (1905); Sebor and Simek: Zeit. Elektrochemie, 13, 113 (1907); Bairsto: Trans. Faraday Soc., 8, 232 (1912); on the behavior of several metal anodes, see Schulze: Drude's Ann., 21, 929 (1906); 22, 543 (1906); 23, 226 (1907); 24, 43 (1907); 25, 775 (1908); Zeit. Elektrochemie, 14, 333 (1908); 18, 22 (1912); Trans. Faraday Soc., 9, 266 (1914).

[5] Schulze: 1. c.

mains so in solutions which do not attack the oxide covering. It is supposed that this film consists[1] of a very thin non-porous layer of oxide, covered by a porous one, with gas occluded in the pores of the outer film. The outer film may slowly dissolve, while the inner one becomes porous and is replaced by a new one formed by the oxygen liberated, breaking through the original film.

Under conditions of high current density, low temperature, and strong sulphuric acid, lead as anode dissolves as tetravalent lead.[2] While we do not know what the potential of the lead is, this is a case of retarded solution, strictly analogous to the passivity of chromium.

A lead anode in dilute sulphuric acid, for instance, becomes covered with lead dioxide, in quantities such that there is no question about the film. The combination is noble, and the film is destroyed by hydrochloric acid. When thus protected by oxide, the lead dissolves only slowly in sulphuric or nitric acid.

Attempts have been made to induce passivity of lead anodically without a visible film.[3] The results were not highly satisfactory, however. One of the experiments with strong nitric acid without the current may be given. A lead rod when dipped in concentrated nitric acid is not so soluble in 25 percent acid as it was before immersion in the former. For instance, two rods suspended in concentrated acid, one for three minutes, the other for one day, showed the following quantities of lead dissolved in 25 percent acid in two hours as compared with a lead rod not treated with strong acid. The surface was the same in all cases. The lead in solution was determined as sulphate.

	Quantity of lead (calc. from sulphate) dissolved in 2 hours
Rod not treated (Blank).....	0.7951 gram
Rod treated 3 minutes.................	0.7900 gram
Rod treated 1 day...............	0.4725

[1] Schulze: Drude's Ann., **28,** 789 (1909).

[2] Elbs and Fischer: Zeit. Elektrochemie, **7,** 343 (1900).

[3] These experiments were performed for us by Douglas and Wendt.

Thus by treating with strong nitric acid, there is a retardation of the chemical solution of lead in dilute nitric acid.

It has been noted that manganese or rather ferro-manganese as anode[1] dissolves with the formation of potassium permanganate, in other words with a valence of seven. The normal reaction of manganese, and caustic soda, for instance, involves the formation of manganous hydroxide. When the current density is raised, permanganate is formed. Attempts to oxidize manganous hydroxide and manganese dioxide at the surface of platinum to permanganate have been unsuccessful. It seems here that we have a case of the formation of the higher oxide when metallic manganese is present, but not in its absence. At any rate we have another case of retarded solution, or solution of the metal with a higher valence, than normal. Thus the manganese as well as the lead have been made passive. It is highly probable that the passive state of this metal is so unstable that it persists only under anodic influences and consequently those who have measured potentials of the metals have said that manganese did not exhibit passivity.[2]

Copper when used as anode in sodium hydroxide becomes passive[3] and is coated with a film of Cu_2O_3.

Zinc[4] develops the passive state both chemically and anodically, in which condition it becomes more noble.

Tungsten,[5] uranium, tantalum,[6][7] molybdenum,[7] vanadium,[8] columbium, ruthenium,[9] platinum,[10] gold,[11] bismuth,[12]

[1] Lorenz: Zeit. anorg. Chem., 12, 393 (1896); White: Trans. Am. Electrochem. Soc., 9, 255 (1906); Kuessner: Zeit. Elektrochemie, 16, 758 (1910).

[2] Zeit. Elektrochemie, 10, 929 (1904); see also Ibid., 11, 755 (1905).

[3] Müller and Spitzer: Ibid., 13, 25 (1907); Müller: Ibid., 13, 133 (1907).

[4] Centnerszwer and Drucker: Jour. Chim. phys., 13, 162 (1915)

[5] Rideal: Trans. Faraday Soc., 9, 281 (1914); Koerner: Met. Chem. Eng., 16, 40 (1917).

[6] Schulze: Trans. Faraday Soc., l. c., p. 270.

[7] Kuessner: Zeit. Elektrochemie, 16, 754 (1910); Marino: Gazz. chim. ital., 35 II, 193 (1905).

[8] Marino: Zeit. anorg. Chem., 39, 152 (1904).

[9] W. J. Müller: Zeit. Elektrochemie, 10, 929 (1904).

[10] Ruer: Ibid., 11, 671 (1905); 14, 309, 633 (1908); Zeit. phys. Chem., 44, 81 (1903).

[11] Coehn and Jacobsen: Zeit. anorg. Chem., 55, 335 (1907).

[12] Poggendorff: Pogg. Ann., 74, 587 (1849).

and cadmium[1] also exhibit the phenomenon of passivity.[2] Summing up now, we find that passivity of metals is developed through or by oxidation processes.

A passive rod or iron may passivate another piece by immersing a sufficiently small surface of the active rod in a solution with the passive rod which is in electrical contact. If the surface of the active rod is too large the whole will be active instead of passive. So far as the facts are at hand, it seems that most passive metals really dissolve slowly, while chromium becomes passive and dissolves less rapidly, namely, with a higher valence. Increase in temperature tends to prevent or destroy passivity. The passive state is destroyed by making the metal cathode or by treating with reducing agents.[3] This process is preceded by a period of induction. Passive iron is made active by scratching or touching with a

[1] Schönn: Zeit anal. Chem., **10**, 291 (1871).

[2] Some papers on the general subject of passivity are given. Bernaoulli: Dissertation, Munich; Caspari: Zeit. phys. Chem., **30**, 89 (1899); Michell· Arch. sci. phys nat., (4) **10**, 122 (1900) (on chromium), Elbs and Nübling. Zeit. Elektrochemie, **9**, 776 (1903); Brauer. Zeit phys. Chem., **38**, 441 (1901) (on chromium); Nernst and Lessing Chem Zentr., (5) 6 II, 241 (1902), Burgess. Trans. Am Electrochem. Soc , **4**, 31 (1903); Foerster and Piguet· Zeit Elektrochemie, **10**, 714 (1904); Muthmann: Ibid., **10**, 521 (1904); F. Fischer: Zeit. phys. Chem , **48**, 177 (1904); Hollis. Proc Camb Phil. Soc , **12**, 253, 462 (1904); Holtz: Physik Zeit., **6**, 480 (1905); Winkelmann. Drude's Ann , **17**, 589 (1905); Sackur: Zeit. Elektrochemie, **12**, 637 (1906), Zeit. phys. Chem , **54**, 641 (1906); Lorenz and Hauser: Zeit. anorg. Chem., **51**, 81 (1906); Jour. Iron and Steel Inst., **4**, 922 (1906); Gordon and Clark Chem. Ztg., **30**, 911 (1906); Lewis: Jour. Am. Chem. Soc., **28**, 158 (1906); Luther: Zeit. Elektrochemie, **12**, 596 (1906); *Zirnilé: Chem. Zeit., 12, 355 (1888)*, Haber and Maitland. Zeit. Elektrochemie, **13**, 309 (1907); Schoch: Trans. Am Electrochem. Soc., **14**, 99 (1908); Kreusler: Chem. Ztg., **32**, 476 (1908); Krassa: Zeit. Elektrochemie, **15**, 490 (1909); Int. Cong. Applied Chem. (London) (1910); Dunstan and Hill: Jour. Chem. Soc., **99**, 1835 (1911); Kistiakowsky: Zeit. Elektrochemie, **16**, 881 (1910); Int. Cong. Applied Chem. (London) (1910); Byers and Voris: Jour. Am. Chem. Soc., **34**, 1368 (1912); Friend: Jour. Chem. Soc., **101**, 50 (1912); Armstrong and Colgate. Jour. Soc. Chem. Ind., **32**, 394 (1913); Byers and Langdon: Jour. Am. Chem. Soc., **36**, 2004 (1914); Rathert: Zeit. phys. Chem., **86**, 567 (1914); Flade: Ibid., **76**, 513 (1911); **88**, 569 (1914); Met. Chem. Eng., **11**, 12, 679 (1913); Young and Hogg: Jour. Phys. Chem., **19**, 617 (1915). On rusting of iron and passivity, see Mugdan· Zeit. Elektrochemie, **9**, 442 (1903).

[3] Flade and Koch: Zeit. phys. Chem., **88**, 307, 569 (1914).

less noble metal (arranging conditions so that the iron may be cathode with sufficient current). There are degrees of activity or passivity, and the transition from one to the other is a gradual one. Passive iron (and presumably passive metal) shows photo-electric fatigue, and some passive metals show electro-static capacities. The appearance of the passive state is exactly as the active state, except in alkaline solutions. A measureable difference in the reflecting power is not found in two pieces of iron polarized cathodically and anodically, respectively.

The passivity of metals has called forth probably more experimental work than any other portion of the science, of the same importance. Especially noticeable is this, since most of the experimenters agree that a satisfactory explanation has not been reached. Faraday's oxide or oxygen theory was generally accepted until Hittorf showed that chromium became passive or noble but still dissolved quantitatively in most solutions as hexavalent ion. The oxide film theory which was developed more fully by subsequent workers postulates that a film of oxide covers the surface of the iron and protects it from the action of the electrolyte. When this oxide is reduced the metal becomes active.[1]

There have been tabulated quite a formidable list of objections to this theory. The following presents the most weighty ones.

In the cases of iron and chromium the oxides must be other than the known oxides, and they must be unstable.

The oxides must be good conductors of electricity.[2]

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[1] A list of papers leaning to this view not given elsewhere follows: *H. von Helmholtz: Messungen und die Fortpflanz. der Reizung in den Nerven, Vol. 2, p. 764;* Heathcote: Zeit. phys. Chem., **37**, 368 (1901); Haber and Brunner: Zeit. Elektrochemie, **10**, 698 (1904); E. Müller and Spitzer: Zeit. anorg. Chem., **50**, 321 (1906); Zeit. Elektrochemie, **11**, 923 (1905); Haber and Goldschmidt: Zeit. Elektrochemie, **12**, 49 (1906); Haber: Zeit. anorg. Chem., **51**, 356 (1906); Haber and Zawidzki: Zeit. phys. Chem., **78**, 228 (1911); Ruer: Zeit. phys. Chem., **44**, 109 (1903); Ostwald: see below; Manchot: Ber. Deutsch. chem. Ges., **42**, 3942 (1909).

[2] Ostwald: *Abhand der Math. phys. König Sächs. Ges. d. wiss., 25, No. 4 (1899);* **26**, *No. 2 (1900);* Zeit. phys. Chem., **35**, 33, 211 (1900); Zeit. Electrochemie, **7**, 635 (1901).

The Passive State of Metals

The

with different valences, is present in quantities depending on the conditions of temperature and other factors. The behavior of a metal anode will depend on the relative concentrations of these modifications. Attempts have been made by W. J. Müller to find evidence for this theory in a consideration of the electron theory of metallic conduction. Hittorf[1] and Byers[2] favor the view that the metal is changed but do not venture a guess at the character of the change. The futility of such a theory is apparent when we consider that Finkelstein assumes that at the surface of iron are present both ferric and ferrous iron. The ferric iron is noble. Ferrous iron dissolves leaving an excess of ferric and the anode is passive. If, however, the conditions are such that ferric is transformed rapidly into ferrous the anode is active for the surface does not become covered with an excess of ferric ions. Müller considers the passive iron to be hexavalent. The cause of passivity is to be sought within the electrode itself. In other words the character of the solution would not change in any way the phenomena of passivity. This being just contrary to what is actually found, and in view of the fact that there is no sudden change in voltage showing the appearance or disappearance of one or another modification, the theory has not been supported. It is also open to the rather serious objection that the whole thing is a fiction of the imagination founded on very little fact, and is very poorly developed.

Le Blanc[3] has developed the so-called "reaction velocity" hypothesis which postulates that the passage of the metal into the ionic state is a reaction accompanied with a chemical change which may or may not be rapid. If slow, the metal is passive, and *vice versa.* The chemical change is either a re-

[1] Hittorf: l. c.

[2] Byers: Jour. Am. Chem. Soc., 30, 1742 (1908).

[3] Le Blanc: Boltzmann Festschrift, 183 (1904); Zeit. Elektrochemie, 6, 472 (1900); 11, 8, 705 (1905); *Abhandlungen der Bunsen Ges., No. 3 (1910)*; "Textbook of Electrochemistry," 283 (1911); Trans. Faraday Soc., 9, 251 (1914); Reichinstein: Ibid., 9, 228 (1914); Sackur: Zeit. Elektrochemie, 10, 841 (1904); Brochet and Petit: Ibid., 10, 909; Bull. Soc. chim., Paris, (3) 31, 742 (1904).

action of the metal with the discharged anion,[1] or, according to Le Blanc, it may be the hydration of the ion, thus:

$$\text{Ion} + \text{water} \rightleftharpoons \text{ion hydrate}$$

When this reaction is slow, polarization sets in until the potential becomes so high that oxygen may separate. This interesting theory, which in general (reaction velocity) expresses one of the properties of passive metals, is based on an assumption highly improbable, *viz.*, that the hydration of the ion takes place slowly when the anode of iron is in sulphates and nitrates, but rapidly in chlorides. Furthermore, after one's credulity is thus strained, it must be believed that the reaction of ion hydration must be rapid or slow in the same solution under the same conditions.

This would occur in chromic acid solution. If iron made passive in air be placed in this solution it remains passive; active iron placed therein remains active.[2] Thus under identical conditions (because by definition there is no difference between active and passive iron) a reaction may be rapid or slow, which is absurd. Such a theory based on assumptions *ad hoc*, should not be taken seriously.

As for the slow reacton of the "discharged ion" with the metal, causing passivity, such a theory is absurd. If active iron is made anode in sulphuric acid, solution of the iron goes on to some extent; the metal then becomes passive, and the solution of the iron drops to a minimum. Suppose we assume that this minimum represents the solution due to the slow reaction above. The iron dissolved more rapidly at first, and we are at a loss to know why its solubility decreased. It may be seen, therefore, that the above-mentioned theory, assuming that anions were discharged, is simply a statement of the proposition, rather than a solution of the problem.

Furthermore, regarding the views of both Le Blanc and Sackur it may be said that iron as anode may be made pas-

[1] Sackur: Zeit. Elektrochemie, **14**, 607 (1908).

[2] Schmidt: Trans. Faraday Soc., **9**, 263 (1914).

sive by opening and closing the circuit at current densities where it would continuously dissolve if the current flows uninterruptedly.[1]   Heathcote says it "behaves as if one could teach it to become passive."   It is absurd to consider that the conditions are changed, by opening and closing the circuit, so that the reaction, of the discharged ion (assumed) with the metal, or of the ion hydration, is slowed down.   Rather, since diffusion is allowed, the reaction should be increased.

Shortly after the above view of the situation was published Fredenhagen developed the so-called oxygen charge or oxygen film theory.[2]   He polarized an anode and found that the polarization potential rose gradually.   There were no sudden breaks in the voltage current curve.   He assumed that the polarization was due to the slow reaction of the metal with oxygen and the oxygen builds up forming an oxygen film over the surface of the electrode.   The investigator assumes the presence of oxygen at the anode, for when hydrochloric acid or chlorides are added and electrolysis carried on, hypochlorite (sic) is obtained.   It is assumed that the discharged chlorine reacts with the oxygen of the film.   It is considered that the oxygen or oxide is present as a solid solution in the metal.   Thus an increase in temperature would drive out this oxygen and render the iron active.   It would explain the negative effect obtained by measuring the reflection of light by the active or passive condition of the iron.

On the other hand, the really serious objection to this theory is that it postulates a slow reaction between a metal and active oxygen.   We know, however, that magnesium is passive and yet it is acted on by atmospheric air.   Iron rusts readily, but we are asked to assume that it reacts only slowly with nascent oxygen.   One would hardly grant that for the sake of argument.

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[1] Heathcote: 1. c.

[2] Fredenhagen: Zeit. phys. Chem., **43**, 1 (1903); **63**, 1 (1908); Zeit. Elektrochemie, **11**, 762, 857 (1905); Mugdan: Ibid., **9**, 442 (1903); Muthmann and Frauenberger: *Sitzungsber. kgl. bayr. Akad.*, *34*, *201* (*1904*); Zeit. Elektrochemie, **10**, 929 (1904); Flade: Zeit. phys. Chem., **76**, 513 (1911).

Tomlinson[1] assumed that the passivity of iron was due to its extreme cleanliness.

Reviving this idea, Foerster[2] assumes that iron is normally passive, and that activity is due to the presence of a catalytic agent. The reasoning according to Grave[3] is not at all convincing. He assumes, however, that hydrogen ion is the catalytic agent. Without going further into an unprofitable theory we may say that Flade and Koch[4] have heated active iron in a vacuum. After heating, the iron was still active which shows that the hydrogen has nothing essential to do with the phenomenon. This result is just contrary to the experiments of Grave, who found that iron heated in a vacuum at 357° C for one-half hour became more noble by 0.1712 volt. This forces us to discard the work of Grave, who also found that iron became passive, or more noble by 0.3122 volt, after heating to a white heat in nitrogen. The contradiction mentioned above, together with the fact that in all of Grave's experiments of heating iron, only when hydrogen formed the atmosphere, was the iron active, -- lead us to believe that in the experiments, the iron came in contact with the air after heating. Thus pure iron, prepared by heating in nitrogen, on being exposed to air would acquire a film of oxide spontaneously. This would protect it and make it more noble in the tenth normal potassium hydroxide used in measuring the potential. In the case of heating in hydrogen, this gas might have protected the metal from oxidation so that a film of the proper thickness would not form.

In view of the fact, too, that no analyses are given of the nitrogen used by Grave, and in view of the fact that it is one of the most difficult gases to obtain free from oxygen, it seems from the simple procedure used, that oxygen would unquestionably be present. We have found that it is a most difficult problem to keep oxygen out of gaseous nitrogen,

[1] Jour. Chem. Soc., **22,** 141 (1869).

[2] *Foerster: Abhandlungen Bunsen Ges., No. 2 (1909)*.

[3] Grave: Zeit. phys. Chem., **77,** 513 (1911); Rathert: Ibid., **86,** 567 (1014); Schmidt and Rathert: Trans. Faraday Soc., **9,** 257 (1914).

[4] Flade and Koch: Zeit. Elektrochemie, **18,** 335 (1912).

in carrying out high temperature work. In fact we have probably never been able to keep out traces of this gas. The slightest trace of moisture in the presence of red-hot iron will certainly give oxide. We feel therefore that it is impossible to accept the statement that iron would become passive if heated in pure nitrogen, especially in view of the fact that the critical experiment upon which Grave bases his theory, has been shown to be wrong.

Having seen that the theories given above are none of them satisfactory as stated and developed, suppose we start at the beginning and see what can be accomplished. All processes of developing the passive state of metals are oxidation processes. The phenomenon must, therefore, be due to oxidation. Oxidation may be considered from four standpoints. These will be considered and discussed in turn. We prefer not to consider the "so-called" "reaction velocity" hypothesis other than a statement of the problem.

In the first place, oxidation from the electrolytic standpoint consists in adding a positive charge to an ion. It might be assumed therefore that the process was one of increasing the valence of the metal at the surface, without effecting chemical combination. This gives us the valence hypothesis in slightly different form. If the valence could be increased, it would be accomplished by adding positive charges to the metal atoms in the solid film. This would mean making ions of them *in situ*. As a matter of fact the passive condition is always preceded by preliminary solution of the metal. When iron is made anode in sodium hydroxide solution for instance, there is a preliminary solution of the metal. Since the amount of preliminary solution may be anything, depending on the conditions (rapid rotation in concentrated nitric acid),[1] there seems to be no reason for assuming that metal of two valences is present or is formed, one of which dissolves leaving the other.

Furthermore, if it is possible to change the valence of the

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[1] See p. 134.

iron, some condition should allow the total conversion of the iron to the noble valence. No case, however, has ever been noted, where more than the surface film has been affected. This ingenious hypothesis seems, therefore, to have been founded less on fact than fancy. We may also add that a close study of the solution and deposition of metals leads us to the inevitable conclusion[1] that when a metal is deposited the ion loses its charge or charges. It is then analogous to metal vapor, or in the atomic state. These free atoms then combine to a complex representing the liquid state, and then to one representing the solid, finally crystallizing. Solution would be the reverse process all along. The complex would dissociate to the atom which would assume a positive charge, and thus become an *ion in solution*. According to our view, to explain polarization in copper sulphate—copper, electrolysis,[2] for instance—we must assume that copper ionizes first, with the assumption of one positive charge. This condition is unstable, and therefore another charge is added. However, if a high current density be used the anode furnishes largely cuprous ions. This is probably due to the fact that with high current density, the migration of acid ions is not sufficient to make the solution at the anode strongly acid. Thus the cuprous ions are more stable and are therefore formed. When the cuprous salt mixes with the bulk of the electrolyte it decomposes separating cuprous oxide or finely divided copper. We believe, therefore, that a metal atom dissolves assuming the smallest number of charges, whereby it may become an ion. If it is stable in this state, it will remain so until complete solution is effected, or until the conditions are changed so that it may become oxidized. Thus iron dissolves as ferrous ion, the oxidation to ferric taking place only after there is no more metal to dissolve.

We are therefore forced to the conclusion that in the solid metal there can be no distinction between ferrous and ferric iron. All particles are the same and the solution or ioniza-

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[1] See Bennett and Thompson: Jour. Phys. Chem., **20,** 296 (1916).

[2] Bennett and Brown: Trans. Am. Electrochem. Soc., **23,** 389 (1913).

tion takes place as ferrous which may or may not be oxidized to ferric, depending on the conditions. The above view of oxidation causing passivity may be dismissed.

2. Oxidation may be considered as removing hydrogen. This cannot cause passivity for Flade and Koch removed the hydrogen from active iron by heating in vacuum, and still found the iron active. ⸲ This view cannot therefore be considered.

3. The next step in the four possibilities is that oxygen might be set free. The process of oxidation might be the generation of an oxygen layer over the surface of the metal. Aside from the fact that we cannot admit that oxygen can be present at the surface of magnesium without entering into combination with it, we find it difficult to see how iron in the air may sometimes acquire the film of gas, to make it passive. This would require that massive metal would condense this gas on its surface. We could see how oxygen could be driven into the metal by the electric current, but we cannot see how, by chemical solution, the gas could accumulate either as a solid solution in the metal which it has not, nor will react with, or as a film over the metal protecting it. This would require the spontaneous decomposition of the passivifying agent separating oxygen. The presence of oxygen is all that is necessary to induce this decomposition. This view cannot possibly be upheld for we know nitric acid does not decompose in the presence of oxygen, in the dark. It could not therefore form a continuous film of oxygen, covering the surface of an iron rod.

4. This brings us then to the last possibility, namely, that the oxidation is the adding of oxygen to the metal in question, with the formation of a definite oxide which on the surface of the metal more or less protects it from action of solution, since the solutions touch the oxide and not the metal itself.

The Faraday hypothesis, however, cannot be accepted, for there are too many valid objections to it, as it has been developed. Probably the most serious objection to the pres-

ent "oxide hypothesis" is that the oxide must be stable under certain conditions, and very unstable when the conditions are slightly changed. Let us inquire into the possibility of stabilizing otherwise unstable products, without a change of conditions of temperature, concentration of solution, etc.

We know that if sodium hydroxide be added to a boiling solution of copper sulphate, the black cupric oxide will be obtained. If, however, a small amount of manganese sulphate be present the black oxide is not obtained but the blue hydrate persists[1] even though the solution be boiled vigorously. The manganese salt is adsorbed by the cupric hydrate and stabilizes it.

Another case strictly analogous to the present problem, is the adsorption of this cupric hydrate by wool Wool boiled in the presence of a copper salt, is dyed green. This is due to the hydrolysis of the copper salt and the adsorption of the cupric hydrate by the wool. The adsorption by the wool stabilizes the cupric hydrate so that it does not decompose and give the black oxide on boiling.[2] By being adsorbed, therefore, we can say that the substance is stable under conditions where it would decompose if alone.

Thus in the case of the oxide which generates the noble potential of passive iron, it is unquestionably unstable as a solid or in solution in water, at ordinary temperatures, for it has not yet been prepared thus. It may be stabilized, however, when in contact with metallic iron. In other words, metallic iron *adsorbs* the oxide, and thus makes it stable.

Adsorption changes with a change in temperature. If adsorption takes place with evolution of heat, it will be decreased by raising the temperature, according to the theorem of Le Chatelier. A decrease in the adsorption of gases by charcoal[3] is found with rising temperature. In the case

[1] Tommasi: Bull. Soc. chim., Paris, (2) **37**, 197 (1882); Comptes rendus, **99**, 37 (1884); Bancroft: Jour. Phys. Chem., **18**, 147 (1914); Blucher and Farnau: Ibid., **18**, 634 (1914).
[2] Bancroft: l. c.
[3] Freundlich: Kapillarchemie, l. c.

of adsorption of dyes by fabric, a number of instances are known where the adsorption passes through a maximum, decreasing beyond this maximum with rising temperature.[1] It is therefore both possible and probable that the adsorption of a higher oxide of iron by iron be decreased with rise in temperature. An increase in the temperature decreases the adsorption of the oxide and that which was stable at the lower temperature becomes unstable and decomposes. The protective oxide would be destroyed, and the metal made active. Besides the decrease in adsorption tending to render the oxide less stable at higher temperatures there is a direct temperature effect on the oxide itself. Several higher oxides of the metals have been prepared at low temperatures. These when brought up to room temperature spontaneously decompose. Thus would the higher oxide of iron tend to decompose with rise of temperature.

It has been urged against the oxide hypothesis, that there was no break in the voltage-current curve, showing the appearance or disappearance of the higher oxide. We cannot see why the adsorbed oxide should give the voltage of massive oxide unless the surface is completely covered. In other words, when passivity is complete the full voltage is reached. It is analogous to the behavior of a platinum cathode in silver nitrate, for instance, with voltage lower than the decomposition voltage. We obtain back electromotive force measurements of values intermediate between platinum and silver. Thus we obtain values intermediate between iron and the higher oxide, as iron becomes active or passive.

Let us consider this also from the standpoint of the well known adsorption isotherm, which with changing concentration is a smooth curve, rather than one with definite breaks in it when definite compounds are formed. The reverse of this adsorption isotherm may be considered as the solubility curve of the adsorbed substance. Since the solubility varies gradually all along, the voltage generated by the ad-

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[1] Bancroft: Jour. Phys. Chem., **19,** 148 (1915).

sorbed oxides would vary continuously. Consequently, there would be no definite breaks in the voltage-current curve.

It has also been urged that an oxide of iron would not give the potential of passive iron. In view of the fact that we know lead dioxide and manganese dioxide are good electrical conductors[1] and give potentials higher than that of passive iron, there is no reason why a higher oxide of iron than those known at the present time should not give such potentials. In fact, we could not explain a low potential if given by reasoning from analogy. The instability of the oxide with a strong depolarizing power in itself requires the generation of a high negative potential.

Now let us state the new theory more fully. Before becoming passive, iron dissolves in such passivifying agents as nitric acid, and sulphuric acid when the current is used. In fact, in all such cases passivity is preceded by a preliminary solution of the iron.[2] This gradually decreases and finally drops to a minimum value, when the iron becomes passive. This preliminary solution of the iron indicates that the phenomenon of passivity is not occasioned by an oxidation of the solid iron surface to the higher oxide directly or *in situ*. If such were the case the passivifying action of nitric acid would decrease as the iron nitrate concentration increased, occasioned by the preliminary solution of the iron. This would follow, for ferric nitrate solution (which is obtained) is not as strong an oxidizing agent as 1.40 nitric acid, for instance. This would mean that 1.40 nitric acid is too strong an oxidizing agent or that iron ion catalyzed the formation of the higher oxide, neither of which is tenable, since active iron does not become passive in chromic acid solution, although once made passive it remains passive therein. Furthermore, if the tendency is to oxidize to the higher oxide *in situ*, a rapid removal of the ferric nitrate would tend to increase the speed of the oxidation and would tend to aid

[1] Haber and Goldschmidt, Zeit. Elektrochemie, 12, 62 (1906), have shown that Fe₃O₁₁ conducts the current, as a conductor of the first class.
[2] Heathcote: l. c.

in passivifying the piece. As a matter of fact, rotation of the piece is known to decrease the passivifying action. We also have found that if a piece of iron wire is fastened in a chuck so as to be "off center," and rapidly rotated, 1.40 nitric acid does not make it passive, but the iron continues to dissolve rapidly.

Since, therefore, the film cannot be formed *in situ*, it must be formed from the solution side. The oxidizing agent must oxidize the iron up to the higher valence, and the metallic surface adsorbs the higher oxide. The iron probably ionizes as ferrous, is immediately oxidized to ferric, and some ions are taken up higher to form the higher oxide. This is then adsorbed by the iron. The rapid stirring, therefore, removes the ferric ions before they can be further oxidized, and therefore the iron remains active.

It may be asked, at this point, why the iron is oxidized to the higher oxide at all when metallic iron is present to dissolve. It might be claimed that the potential would never rise high enough to accomplish the oxidation. As the speed of a process is increased, the voltage at which the process is carried out is likewise increased. Furthermore as the concentration of iron ions in the solution increases it requires more work to force more into the solution. The concentration of iron ions is probably very high over the surface film of the anode under conditions for the development of the passive state. Under these current conditions, the iron ions sent into the solution are probably more than equivalent to the sulphate ions brought up to the anode in the case of the development of passivity as anode in sulphuric acid. The hydroxyl, or oxygen, ions will probably carry a part of the current. This means that at these rather high current densities, there will be a partial formation of oxide or hydroxide of iron, which as a film would further tend to hinder solution of the anode. Three factors, namely, the increase in the speed of the process, the building up of the products of the reaction, and the development of a basic condition with a film of a normal oxide or hydroxide of iron, tend to raise

the voltage of the anode process and therefore tend to develop conditions for the formation of a higher oxide which may protect and make the metal more noble. By rapidly stirring, these conditions are overcome. Moreover, when the process of solution as anode is slow, the conditions above are not developed.

When the current density is low iron may dissolve and diffuse away, the potential never becoming high enough to form the higher oxide.

According to this view, the Luckow phenomenon, referred to above, could not be expected to take place. When the iron ions which have been oxidized to the higher valence are removed from the surface of the iron they are unstable and break down. Suppose we consider a strong solution of nitric and hydrochloric acid, with an iron anode. Suppose also that there was formed ferric chloride which diffuses back, and let us assume, for the sake of argument, that the nitric acid oxidized the ferric iron to the higher oxide. In the absence of hydrochloric acid it could not exist in measurable quantities at ordinary temperatures unless in the presence of iron (metal). Another cause of its decomposition would also be found in the hydrochloric acid present. Just as hydrochloric acid decomposes lead and manganese dioxides, so would it decompose the higher oxide of iron. No passivity can be obtained when this acid is present.

Iron which has been made passive and is noble may become less so by standing in air or by being placed in a vacuum. This follows from the theory above. The higher oxide gradually dissolves in the liquid film, and decomposes. When the piece becomes dry it is stable and can be kept so practically indefinitely. The instability wet is therefore due to solubility of the oxide. Thus the metal is said to dissolve slowly in the reagent which develops and maintains passivity. In potassium nitrate solution the life of the adsorbed layer is very short. Here as well as in air and vacuum, the passive state is not being maintained by the formation of more of the higher oxide as in the case of strong nitric acid. The phenom-

enon is therefore dynamic as has been said above. In the case
of some solutions where the passive iron becomes rapidly
active, it may not be due entirely to a solution or decom-
position of the oxide. The iron may strongly adsorb one or
more of the ions in the solution and thus displace the ad-
sorbed oxide. We know of many cases of such displacement
in adsorption. When arsenic sulphide[1] is coagulated with
barium chloride and the precipitate treated with calcium
nitrate, no barium is left in the precipitate, it being quan-
titatively replaced or displaced by calcium.

Thus the adsorption of the higher oxide may be de-
creased until the potential is changed to positive and the
iron becomes active. Passive iron does not have its oxide
film reduced by air, but it merely decomposes, liberating
oxygen,[2] just as many substances liberate oxygen by being
oxidized to higher oxides which decompose, the substances
going back to the original oxide.

The fact that iron as anode may be passive, but when
the current is broken it becomes active, is in accord with the
theory. As long as oxide is being formed and adsorbed
the iron is passive. When the forming of oxide ceases the
reverse reaction of solution and decomposition predominates
and the iron becomes active. In the same way if this reaction
is slow only a small amount of oxide must be formed to coun-
teract it, and therefore after passivity has been accomplished
at the anode, a very small current serves to maintain this
state.

The reason iron is not passivated by chromic acid chem-
ically, but is as anode in this acid, and furthermore, when
passive will remain so in the acid, is found in the fact that
as iron dissolves in chromic acid hydrogen is set free *at the
surface of the iron*. This lowers the oxidizing potential so that
the higher oxide is not formed. When, however, the hydrogen

[1] Linder and Picton: Chem. Soc. Jour., **67**, 66 (1895); see also Freundlich:
Kapillarchemie, on organic acids displacing each other.
[2] Unpublished work. Cf. Müller and Spitzer: Zeit. anorg. Chem., **50**,
322 (1906); see also Foerster and Müller: Zeit. Elektrochemie, **13**, 133 (1907).

is liberated at the cathode rather than at the surface of the iron, the anode becomes passive. The chromic acid is sufficient oxidizing agent to maintain passivity of the iron and, if hydrogen is kept away, it possibly would passivify active iron.

The objection raised by Königsberger and Müller that attempts to show the presence of an oxide film by the difference in the reflecting power of the anode and cathode of iron, is not valid on any ground. In the first place adsorption by solids may take place without markedly changing the appearance of the surface. In the second place there are instances of the presence of oxides where optical means do not distinguish them. Lastly, however, the most serious objection to the work of the above experimenters is that they compared the anode with the cathode as to reflecting power of light. We now know that the liberation of hydrogen[1] at the surface of a cathode results in roughening and darkening the surface so that less light is reflected. Especially would this be true with iron where the adsorption of hydrogen is high. In driving this hydrogen into the metal, the surface must be disturbed. These measurements were therefore made on pieces of metal whose surfaces were unquestionably the same; one, however, was made *matte* by use as cathode, the other as anode.

Now as to the various ways in which activity may be re-established, there is very little that need be said. When passive iron is placed in water or other solutions which tend to induce activity, it is only necessary to remember that the cause which produced passivity has been removed and therefore if the absorbed oxide decomposes at all, activity must result. Adsorbed substances can be washed out by certain liquids, depending on the substance absorbed. This may be by straight partition or by replacement. At any rate the concentration of the adsorbed substance would always be zero in the solution, for as soon as it is washed out it would

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[1] Newbery: Jour. Chem. Soc., **105**, 2426 (1914).

decompose. Thus the iron would be exposed, or become active. Any reducing agent would actually reduce the oxide. Thus reducing agents tend to destroy passivity.[1]

In the same way making the piece cathode would reduce the oxide and render the metal active.[2] Touching with a base metal like copper, zinc or iron, makes the passive metal cathode, reduces the oxide, and renders the metal active. Scratching exposes a certain amount of the metal surface. This gives a local cell in which the iron in the scratch acts as anode while the oxide acts as cathode. Either the scratch is of such a nature that the current density is low (at the iron bared by scratching) so the iron dissolves as anode not becoming passive again or during the operation of scratching sufficient reduction has occurred at the cathode (the part of the piece not scratched) so that the whole thing becomes active. Both the reduction during the process of scratching, and the fact that the critical current density is not reached on the anode area, probably play a part in the activation by scratching.

The former is indicated by the fact that when a passive dry rod is scratched, and then dipped in acid, it becomes active only on the part scratched. There is certainly no reduction during scratching. This experiment is not absolutely conclusive, however, for we are dealing with a dry film, and therefore the conditions are not the same as with the wet film. In the case of the wet film, the whole piece does become active, and there is probably reduction during scratching, for every condition for a local cell is fulfilled. Iron is continually exposed, and therefore must act as anode, the oxide film being cathode.

After the disturbance due to scratching has ceased the iron will probably continue to function as anode. When a scratch is made the acid which finds its way to the iron must be made dilute by the solution of the iron in it. This tends to decrease its oxidizing power. Furthermore the scratch

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[1] Flade and Koch: Zeit. phys. Chem., **88**, 307 (1914).
[2] In this connection see Hart: Trans. Am. Inst. Min. Eng., May (1886).

is probably narrow and the cross-section of the acid film is small. Thus the electrical resistance in the circuit of the local cell would be high and therefore the current would be low. Thus a low anode current density in the local cell.

Iron ———— Nitric Acid ———— Higher Oxide, Iron, should develop activity.

An experiment was tried to show that cutting the current density down below the critical value at a small spot would cause the rod to become active. Accordingly a rod was made passive about two inches up from the end. About the same distance further up, a filter paper was wrapped around the rod. By immersing the passive end first the second area was made passive. When the edge of the filter paper was reached the whole became active. This occurred even though the filter paper was wet with 1.20, 1.40 sp. gr. nitric acid, with water or left dry. The current density is low due to the resistance of the diaphragm separating the active and passive portions. Iron continues to dissolve and shortly the passive metal is made active. When the area under the paper was covered with an oxide film by heating in the oxidizing flame of the Bunsen burner, immersion in dilute (1.20) nitric acid did not cause activity over any part of the rod. When there was no anode of iron, in.other words, there was no activity. In scratching passive iron the important effect is the development of a current of low density at the surface of the iron bared, with the adjacent areas acting as cathode, having the oxide layer reduced, while the iron (anode) continues to dissolve.

The pulsation effect is easily explained on the basis of this theory. It is due to local inequalities. One spot acts as anode, the remainder of the piece as cathode. Some time is required for the oxygen to oxidize the iron to the higher oxide and have it adsorbed by the iron. There would be less time lag at the cathode where hydrogen is depolarized by the oxide. This lag in time at the anode would cause the cathode reaction to go further than it would if no such lag occurred. When the anode finally becomes noble, the cathode is less

noble and the current changes, and so on, giving rise to pulsations. It would probably be impossible to passivify two pieces of metal connected together without having an interchange of passivity and activity, with a consequent flow of current back and forth. This is due to local difference in the metal, namely, differences in the physical state of the pieces of metal.

Nichols and Franklin[1] claim that in the magnetic field iron becomes active. Byers[2] has shown that in the magnetic field a higher anodic current density is required to develop passivity, than when the field is not operative. Both investigators are probably right. Nichols and Franklin used iron filings, and we have shown that if filings are made passive and placed between the poles of an electro-magnet, and the current turned on, the filings become active. This is due to one piece scratching another, caused during orientation of the particles of iron when magnetized. When a solid piece of iron is passivated in 1.40 nitric acid, and placed in the field, it does not become active. There is probably a tendency to activify, however, which is measured by the increase of anode current density required to make the iron passive when under the influence of the magnetic field. This can be accounted for by the effect of the field upon the metal itself. The field must pulsate, causing a pulsating effect in the particles at the surface of the metal. This would disturb the adsorbed film and therefore tend to expose the metal. The field also effects a considerable stirring of the solution. This decreases the tendency to passivify and Byers concludes that this latter effect is sufficient to explain the difference.

According to the view of passivity taken, it becomes easy to explain certain facts which have been known for a long time. In the experiment of Herschel, for instance, where an iron rod was divided into two parts by a band of wax

[1] Nichols and Franklin: l. c.

[2] Byers and Darrin: Jour. Am. Chem. Soc., **32,** 750 (1910); Byers and Morgan: Ibid., **33,** 1757 (1911); Byers and Langdon: Ibid., **35,** 759 (1913).

around the rod at the center, after inducing passivity on both ends of the rod, activity was restored on one end only when that was touched with copper, the whole being in air; when both ends were in acid and one end touched, the whole becomes active. When the rod is touched with the base metal in air, it becomes cathode, the base metal anode, the film of acid being the electrolyte. Since, however, the acid does not wet the wax, thereby forming no film over it, the cathode area extends over one end only. Consequently only one end, namely, the end touched, becomes active. When, however, the rod is immersed in the acid the electrolyte is continuous and both ends of the rod may now act as cathode. Consequently both ends become active under these conditions.

When a piece of passive iron, held in air with a film of acid over its surface, is touched with a base metal or scratched it becomes active, the activity spreading gradually so that it can be followed by the eye. This slow development of the active state is due to the fact that the electrical resistance of the film of acid is high. It seems therefore that an area is made active by an adjacent portion acting as anode, and so on until the whole is active. In other words, the quantity of current flowing from the end touched to the opposite end of a piece during the operation is negligible, due to the high resistance of the acid film.

When, however, the piece is immersed in acid and touched, there is no such gradual spread of activity as noted above, but the whole becomes active practically at once. Here the acid (electrolyte of the local couple) is a good conductor, offering practically no resistance to the passage of the current. The current is therefore more uniformly distributed and the spread of activity is more rapid. In some cases it can hardly be followed by the eye.

Schönbein's experiments are also explained simply. Using the source of current at his disposal, he could obtain passivity anodically under the conditions of concentration of acid, etc., only when he closed the circuit by lowering

the iron rod into the acid. When it was closed otherwise the current density was not so high as when the rod was lowered into the acid. It is very probable therefore that the critical current density was reached in one case and not in the other. By lowering, the rod became passive progressively. This is made possible since a very small current serves to maintain the passive state, once it has been developed.

It was also noted that if the passive iron was touched with the cathode of platinum for instance, it became active. This is just reversed from the behavior when no current flows. It is due to the fact that the hydrogen separated at the cathode, which is touching the passive iron, reduces the oxide and the piece becomes active. In other words, the action is the same as iron in chromic acid. It remains active so long as hydrogen is liberated at the surface of the metal. When it is removed to the cathode away from the iron, the latter becomes passive.

In "transmitting" passivity to other rods in electrical contact, and dipped in the same acid, or in passivifying more of a rod by immersing, passive end first in acid, Schönbein noticed that the whole arrangement was passive or active, depending on the relative areas of the surfaces of the passive and active iron. Here it must be remembered that there is a definite quantity of the oxide formed, depending on the conditions. This can depolarize a certain quantity of hydrogen, and leave enough to protect the iron from vigorous action of the acid. When too much of the oxide film is used up, the whole will become active. This is accomplished by the use of too much anode surface. In other words, before the large anode can be made passive, the oxide on the cathode portion is used up, and the whole is active. When the anode area is less, it is evident, the whole will become passive. We have found that if a rod is made passive in 1.40 nitric acid, an active surface considerably greater than the passive area can be rendered passive by dipping carefully in 1.20 acid. When the active surface becomes too great the whole becomes active.

It has been noted by Heathcote, that if passive iron is touched with a base metal the pulsation of activity is down and back and not up and back to the point touched. This is simple—when a rod is held vertically in air with an acid film over it, this film is thickest at the lower part of the rod because gravity tends to pull it down. There is, therefore, less resistance to the flow of current down than up and con- sequently more current will flow down, and the activity will begin at a point contiguous to and just beneath the zinc. Thus this portion also acts as anode and the activity spreads down rather than up because the upper part acts more like a dry rod. The range of passivity would then spread back to the zinc and the operation be repeated.

When the passive rod is disturbed under the surface of the acid, the tendency for pulsation would also be down and back, for any ferric nitrate formed will run down the rod, since the density of the solution is greater. The depolar- ization or oxidation power of the solution below will be less than that above the point disturbed, and therefore the same current would induce activity sooner below than above the point touched. The resistance of the electrolyte is not a factor here. It has also been noted that the potential of passive iron is numerically lower in an acid solution con- taining ferric nitrate than in the acid without the iron salt.

Heathcote has also noted that iron can be made passive in sulphuric acid at current densities below the critical value, if the circuit is opened and closed intermittently. This is probably due to the fact that while the current is flowing, and iron ionizing from the surface, the adsorption of the higher oxide is disturbed. This may be occasioned. by the direct change of surface by solution of the iron, or probably by a change in the rate of removal of the oxide formed in solu- tion. When the rate of solution of iron is cut down, the rate of removal of the anode product by the flow of the more concentrated solution down the anode surface is decreased. Thus more time is given to adsorb the oxide. By opening the circuit and decreasing the disturbance at the surface such

oxide as has been formed may be adsorbed. Thus partial passivity has been induced, where no such effect would have been obtained if the surface disturbances had been maintained. By repeating the operation added increments of the adsorbed oxide are obtained until finally passivity is induced.

Fredenhagen has noted that a passive iron anode yields a substance when chlorides are added, which evolves oxygen. He concluded that it is hypochlorite, and is occasioned by the interaction of the *oxygen film* at the iron anode, with the discharged chlorine. Such an assumption is not needed, since we know that hydrochloric acid (which would be formed at the anode) decomposes higher oxides (PbO_2 and MnO_2 for instance) and that chlorine (which might be set free at the anode) evolves oxygen from higher oxides (H_2O_2 for instance). The latter is probably a direct replacement just as zinc replaces copper ion from sulphate solution. This is now under investigation.

Having decided that the facts of passivity can best be explained by the assumption of an adsorbed film of a higher oxide of iron than is now known, it only remains to show what the oxide is.

It is noted[1] that as anode in dilute alkali, iron gives a bluish green solution, at boiling temperatures, before passivity sets in. When the anode is passive, it is coated with a black deposit of velvety appearance.

Müller and Spitzer[2] have shown that from an alkaline iron tartrate solution a reddish brown deposit may be obtained at the anode, which gives very nearly the potential of passive iron. They say that sufficient quantities could not be obtained for analysis. In other words, in small concentrations this oxide becomes stable in alkaline solutions even though iron is not present. It is probably adsorbed by the brown oxide which makes up the mass of the deposit.

Armstrong and Colgate[3] have shown that when iron is

[1] Krassa: Zeit. Elektrochemie, **15**, 490 (1909).
[2] Müller and Spitzer: Zeit. anorg. Chem., **50**, 353 (1906).
[3] Armstrong and Colgate: Jour. Soc. Chem. Ind., **32**, 394 (1913).

dipped in a sulphuric acid solution containing hydrogen dioxide, it is covered with a black deposit. When removed, washed with water and then dipped in hydrogen dioxide alone, the deposit is changed to red or to ordinary rust. They have also noted that an iron anode in sulphuric acid is black previous to passivity. It clears up and becomes passive. It is probable, therefore, that larger quantities of the higher oxide are formed than are used in inducing passivity, or than are adsorbed.

The composition of this oxide under conditions where iron is passive will probably have to be determined indirectly. As a starting point, however, it seemed best to select a solution where we know the iron is in a higher state of oxidation than ferric, and see if suspending a piece of iron in this solution would not cause it to adsorb the oxide and be passive. Accordingly potassium ferrate was prepared by grinding intimately 3 parts of potassium nitrate with 2 parts by weight of powdered iron. This was then heated to a red heat when an energetic reaction went on evolving quantities of fumes. The mass was cooled and digested with cold water. A dark amethystine solution resulted when the reaction occurred in the proper manner. A few times, due to imperfect grinding and mixing of the original materials, a green solution, probably ferrite, was obtained.

An iron rod was dipped in the amethyst-colored solution and allowed to remain for a short time. It was then carefully removed and dipped in distilled water, and finally tested for passivity by dipping in 1.20 nitric acid according to Heathcote. The rod did not dissolve, and was therefore passive. Thus the oxide cannot be higher than FeO_3, because this oxide develops the passive state when the metal is placed therein.

It only remains now to mention one or two facts concerning chromium especially. Chromium we have seen dissolves as anode when passive as hexavalent ion, thus differing from iron. When active it dissolves as bivalent ion. The active condition is unquestionably the untrammeled solution of the anode, the atom assuming two positive charges.

The oxidation to a higher form, when passive, shows that there is some interference under these conditions. The potential is higher, due most likely as in the case of iron, to an oxide film, since the same objections apply to the several theories in the case of chromium as with iron.

Here also it seemed best to induce passivity as was done in the case of iron with potassium ferrate. Chromic acid and sodium chromate were taken. In both solutions chromium, which dissolved readily in hydrochloric acid, became passive after about five minutes' immersion and then washing with water. It did not dissolve in the concentrated hydrochloric acid for several minutes. In this case, therefore, the oxide cannot be higher than CrO_3, for this oxide induces the passive state. Since this oxide is soluble it is probable that the metal forms with the chromate radical chromium chromate,[1] which forms the film, the composition of the oxide being CrO_2. Since iron replaces hydrogen from chromic acid, chromium certainly would. The product CrO_2 would therefore be formed immediately which when adsorbed would make the metal passive. Now when this is anodically polarized CrO_3 is formed by oxidation, and being soluble, is dissolved. Thus chromium when passive dissolves as hexavalent ion. In the case of iron the higher oxide is not readily soluble, and therefore the solution of the iron is not quantitative according to Faraday's law.

At this point attention should be called to the analogy of chromium to lead. Lead unquestionably becomes passive due to the protecting film of lead dioxide. In this case, however, it is stable and every one admits its existence and protection as a film over the lead. However, when the temperature is low and the concentration of sulphuric acid high[2] the lead dissolves as tetravalent ion.

We have noted that chromium dissolves in hydriodic acid. As in the case of iron in chromic acid, hydrogen is sep-

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[1] See Storer and Elliot: Jour. prakt. Chem., **90**, 288 (1863); Carveth and Curry: Jour. Phys. Chem., **9**, 375 (1905).

[2] Elbs and Fischer: l. c.

arated at the surface of the metal. This cuts down oxidation so that oxide films cannot be formed.

When, however, the hydrogen is separated at the cathode, the chromium being anode, the latter becomes passive, probably being covered with CrO_2 due to depolarization of what oxygen was present. The iodine is liberated at a low potential, so that the oxidation tendency is low at the anode. In this way the film is not oxidized to CrO_3 and therefore does not dissolve. The chromium, therefore, becomes indifferent, like iron when made anode in potassium iodide. Hittorf's so-called *"experimentum crucis"* is not therefore in any degree such. The conditions are the same with the exception that hydrogen is present in one case and not in the other as has been shown above. This is more than sufficient to explain the different behavior for we know that nascent hydrogen will reduce the oxides which render these metals passive.

From the above the following may be concluded:

1. The general field of passivity, especially that of iron and chromium, has been reviewed.

2. References to previous work have been appended.

3. The passive state of metals is really a slowly dissolving state.

4. Some metals, chromium, magnesium, and manganese, for instance, dissolve as anode when passive with a higher valence than when active.

5. The different behavior of chromium and iron (representing the two types of action) as anodes cannot be explained on theories heretofore put forward.

6. All these theories are objectionable.

7. Oxidizing conditions develop passivity.

8. Reducing conditions develop activity.

9. In alkaline solutions, passivity is many times accompanied by a visible film over the surface of the anode.

10. There are no facts which would support the view that passivity is due to one cause in alkaline, and another cause in acid solutions.

11. In all cases, passivity is due to oxidation.

12. Oxidation in the sense of (1) increasing the valence, (2) removing hydrogen, or (3) of adding oxygen as a film, have been shown to be untenable.

13. The formation of an oxide as the result of oxidation is arrived at by elimination.

14. This oxide forms a film over the metal by being adsorbed by it. This film protects the metal, and gives its properties to the metal surface.

15. This oxide is unstable in most cases, but is stabilized by adsorption by the metal.

16. The oxide in the case of iron is higher than known oxides, but not so with chromium.

17. The nobility of the surface, the gradual change of electromotive force, and the instability at elevated temperatures is satisfactorily explained by this hypothesis.

18. The quantity of oxide required to protect the surface is very small.

19. In the further oxidation of chromium as anode the higher oxide, CrO_3, is formed and chromium dissolves as hexavalent ion, since this oxide is soluble. Iron does not dissolve because any higher oxide which may be formed is not soluble readily. The quantity of iron that dissolves is due to the straight solution and decomposition of the higher oxide. This is not quantitative according to any reasonable valence.

20. The oxide in the case of chromium is not higher than CrO_3, and is probably $CrCrO_4$ or CrO_2.

21. That in the case of iron is not higher than FeO_3, and may possibly be FeO_2, similar to chromium.

22. Passivity of lead has been shown where there was no visible film.

23. The action here is similar to lead where there is a visible film of oxide.

24. Passivity in all cases, therefore, is the coating of the metal, by adsorption, with a film of a higher oxide which, being more noble than the metal, protects it from the action of the solution.

25. We measure the electromotive force of the oxide instead of the metal.

26. According to this view all the facts of passivity are easily explained.

27. Many conflicting experiments have been explained and thus brought into line with facts.

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THE ABSORPTION COEFFICIENT OF SOLUTIONS OF COBALT CHLORIDE IN WATER AND VARIOUS ALCOHOLS FOR MONOCHROMATIC RADIATION.[1]

BY E. O. HULBURT, T. F. HUTCHINSON, AND H. C. JONES

Experiments have shown that in the case of certain solutions the absorption of monochromatic radiation may be represented by the formula

$$I = I_0 \times 10^{-\alpha t} \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots (1)$$

where I_0 is the original intensity of the radiation. I is the intensity of the radiation after passing through a layer of solution of thickness t millimeters, and α is a constant for the solution in question called the *absorption coefficient* of the solution for the specified frequency of radiation.

Experiments have also shown that different values of α are obtained if there is any change in:

(a) the nature of the solvent or of the dissolved substance,
(b) the concentration of the solution,
(c) the temperature,
(d) the wave-length of the radiation, etc.

To solve the problem of light absorption in solutions it is necessary to determine the explicit form of the relation between the absorption coefficient α, and the quantities of which it is a function. At the present time our knowledge is far too meagre to indicate more than a qualitative idea of the nature of this relation.

In the present investigation α has been measured in those regions of the spectrum where the pure solvents possess appreciable absorption. It is assumed that the total absorption of the solution is the sum of two parts, the first being the absorption due to the presence of the salt, the second being the absorption due to the pure solvent. In calculating this

second part, it is assumed that the absorption due to the solvent is the same as it would be if there were no dissolved salt present. We, therefore, write

$$\alpha = Ac + \alpha_0$$

where α_0 is the absorption coefficient for the pure solvent, c is the concentration in gram-molecules of salt per liter of solution, and A is called the *molecular absorption coefficient* of the salt in the solution. From this relation we get

$$A = \frac{\alpha - \alpha_0}{c} \quad \dots\dots\dots\dots \ . \ \dots\dots\dots (2)$$

The present investigation consisted of a systematic and thorough study of the absorption coefficient α. This quantity has been measured at intervals of $20\mu\mu$ to $40\mu\mu$ throughout the region of the spectrum from $600\mu\mu$ to $1300\mu\mu$ for many solutions. The work has been restricted to a study of inorganic salts in aqueous and alcoholic solution. All the measurements have been carried out with solutions at room temperature. The values of α, when plotted as ordinates against the corresponding wave-lengths as abscissas, form the *absorption curve:* For each salt a series of solutions varying in concentration from saturation to moderate dilution were prepared, and the absorption curve has been drawn for each solution. From the measured values of α and α_0, and from the known value of c, A has been calculated for each wave-length by means of formula (2). The values of A for a given wave-length have been plotted as ordinates against the corresponding values of c as abscissas. The curves thus formed will be referred to as the *A-c curves*.

If experiments with any solution show that the relation between α and c is a linear one, and therefore that A in formula (2) is a constant, the A-c curves for such a solution are straight lines parallel to the axis of abscissas. Previous researches[1][2] have shown that in general the A-c curves are not straight lines parallel to the axis of abscissas, or, in other

[1] Sammlung chemischer und chemisch-technischer Vorträge, **9**, 1 (1904).
[2] Proc. Roy. Soc. Edinburgh, **33**, 156 (1912–13).

words, that A is not a constant.[1]   It was the purpose of the present investigation to determine the form of the A-c curves.

The chlorides, nitrates and sulphates of cobalt, nickel, and chromium, and a few other salts, have been studied in this investigation.   This paper is a report on the results of the work on a single salt, cobalt chloride.

Apparatus—The apparatus used for determining the light absorption coefficient has been developed by previous workers in this laboratory.[2] The arrangement of the apparatus is shown in Fig. 1. The light from a Nernst glower, g, run at 110 volts on 0.8 ampere direct current from a constant potential storage battery, was rendered parallel by a lens, l_1, 3.8 cm in diameter and with a focal length of 20 cm. The light after passing through cell k' was focussed on the slit A of the spectrograph by a second lens, l_2, 3.8 cm in diameter and with a focal length of 20 cm.   A shutter, s, was placed between the glower g and lens l_1, by means of which the light could be turned on and off.   The optical system thus far described, consisting of the glower, the two lenses, l_1 and l_2, and the cells, was held by a solid metal frame work, and was perpendicular to the plane of the drawing in Fig. 1.   The light after passing through the lens l_2 was reflected on to slit
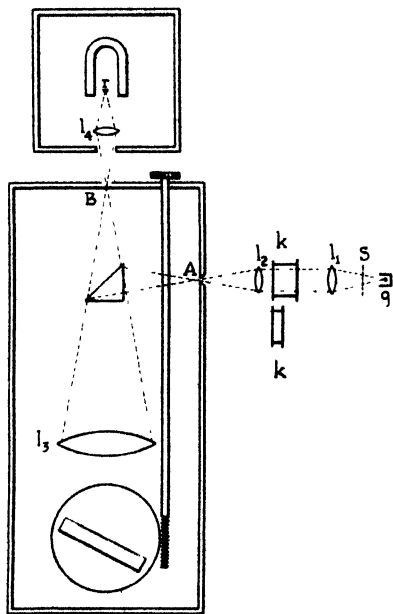
Fig. 1

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[1] Beer has stated (Pogg. Ann., 86, 78–88 (1882)) as a result of his experiments on aqueous solutions of inorganic salts that A is a constant with respect to c.   This "law" of Beer has been shown to be the exception rather than the rule, and therefore in this paper no reference has been made to "Beer's Law."

[2] Carnegie Inst. of Wash., Pub. 190 and 230.

A by a right-angle glass prism (not shown in Fig. 1) close to slit A.

The spectrograph consisted of the Littrow mounting of a plane grating. The grating had a ruled area 6 cm by 7.5 cm and was ruled 15000 lines to the inch. The cone of light from slit A was reflected by a right-angle glass prism through the large achromatic lens l_3, 10 cm in diameter and with a focal length of 75 cm. The spectrum was brought to a focus at slit B. The grating possessed a bright first order, and this first order spectrum was used throughout the present work. The dispersion was such that with slit B one millimeter wide a "monochromatic beam" of light containing a wave-length range of 20 A, or $2\mu\mu$, passed through. In this work both slit A and slit B were always one millimeter in width. The correction for finite slit-width was negligible. The grating was mounted on a turn-table which was rotated from the outside by a worm-screw, thus causing various wave-lengths to pass through slit B. The monochromatic beam of light from slit B was focussed by a lens, l_4, 35 cm in diameter and with a focal length of 6 cm on the junction of the radio-micrometer.

The solution for which α was to be determined was placed in two glass cells exactly alike in all respects, except that one cell was thin and the other thick. The energy, I, of the mono-chromatic beam of light after passing through the thin cell containing a thickness, h, of the solution, and the energy, I', after passing through the thick cell containing a thickness, h', of solution, were measured in arbitrary units, *i. e.*, deflections of the radiomicrometer. If the initial intensity, I_0, of the light falling on the cell was the same in each case

$$I = I_0 \times 10^{-\alpha h}$$
$$I' = I_0 \times 10^{-\alpha h'}$$
$$\alpha = \frac{1}{h' - h} \log \frac{I}{I'}$$
$$\text{or } \alpha = \frac{1}{t} \log \frac{d}{d'} \dots \dots \dots \dots \dots \dots \dots (3)$$

where d and d' are the deflections produced by I and I',

respectively, and t is the difference in thickness in millimeters of the two cells. This method eliminated all corrections for reflections from the glass surfaces, and thus gave α directly.

Results

Cobalt Chloride in Water (Figs. 2, 2a)—Twenty-three solutions were prepared varying in concentration from $c = 3.23$ to
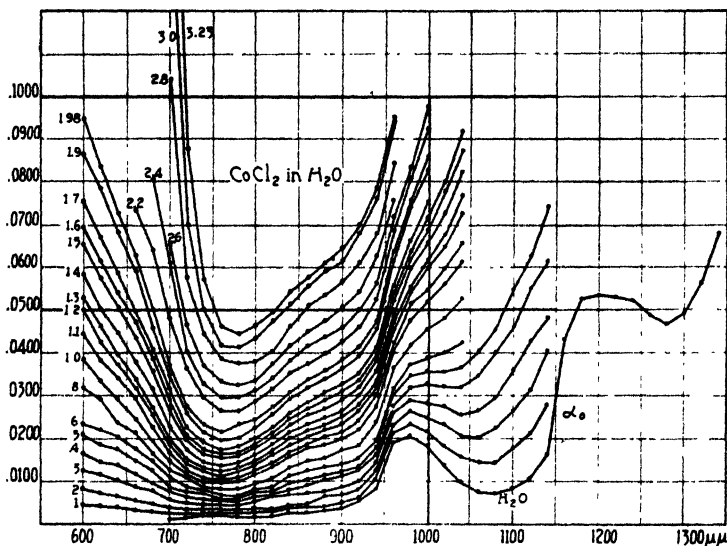
Fig. 2
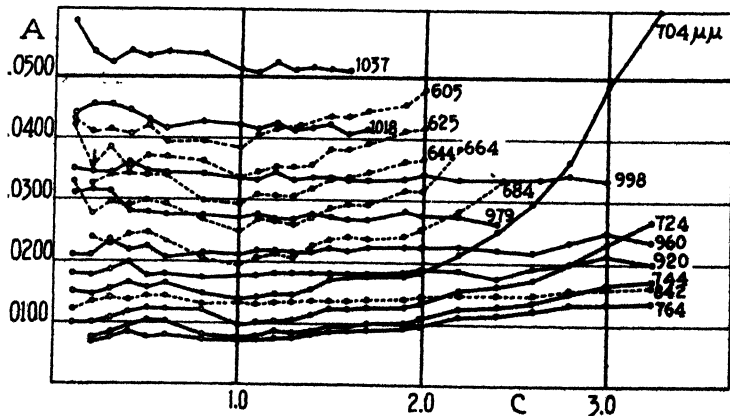
Fig. 2a

$c = 0.1$. The more concentrated solutions were quite stable and showed no signs of decomposition even after standing in the bottles for several days. In the more dilute solutions, however, there appeared a flocculent precipitate which increased their absorption materially. On this account a second set of solutions whose concentrations varied from $c = 1.0$ to $c = 0.1$ were prepared, and the results of the measurements of these appear in the figure.

The absorption curves include the long-wave side of the yellow-green cobalt absorption band and the short-wave side of the infra-red band, and show the region of transmission between the two bands. The minimum of absorption is at $764\mu\mu$.

The A-c curves for wave-lengths $605\mu\mu$ to $764\mu\mu$, inclusive, which lie on the edge of the yellow-green band, show that A decreases in a marked manner with dilution, reaching a minimum value at about $c = 1.0$. Below $c = 1.0$ A experiences a slight increase.

The A-c curves for those wave-lengths in the region of transparency, from $842\mu\mu$ to $979\mu\mu$, are straight lines parallel to the axis of abscissas, showing that in this region A is constant for all concentrations. For wave-lengths greater than $979\mu\mu$, which lie on the edge of the infra-red band, A is a

TABLE I

A for Cobalt Chloride in Water

Wave-length	$c = 0.65$		$c = 3$ 10	
	Houston	From this work	Houston	From this work
$645\mu\mu$	0.041	0.0340	—	—
684	0.024	0.0232	0.200	—
720	0.031	0.0123	0.041	0.0330
750	0.028	0.0090	0.037	0.0150
794	0.028	0.0109	0.016	0.0138
850	0.028	0.0147	0.018	0.0165
910	0.028	0.0175	0.029	0.0198
980	0.040	0.0275	0.038	—
1070	0.070	0.0762	0.074	—

constant within the error of experiment. The two band edges in question are thus seen to behave quite differently as dilution proceeds. Houston[1] has drawn the absorption curves for two solutions of cobalt chloride in water; and Table I shows the comparison between Houston's values and the values found in this work.

The agreement between Houston's values and the values of A found in the present investigation is far from satisfactory. However, both sets indicate similar changes in A with c.

Cobalt Chloride in Methyl Alcohol.   (Figs. 3, 3a)

Seven solutions were prepared varying in concentration from $c = 0.7$ to $c = 0.1$. The solutions appeared to keep very well, and no such precipitate was formed as was noticed in the water solutions. The absorption curves show that the character of the absorption of the alcohol solutions was quite different from that of the water solutions, the absorption curve for the alcohol solution being shifted toward the red,
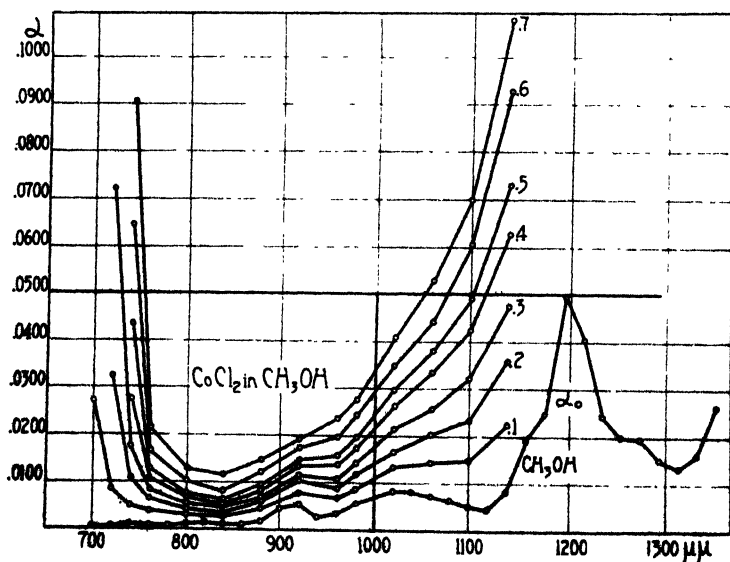
Fig. 3

[1] Proc. Roy. Soc. Edinburgh, 31, 521 (1910–11).

so that the minimum of absorption was now found at $842 \mu\mu$, the shift thus amounting to about $80 \mu\mu$. The shift toward the red of the edge of the band in the green was sufficient to make this band absorb nearly all of the visible red light. (Instead of speaking of the "shift of a band," some have preferred to speak of the bands in the different solvents as entirely different bands.) As a consequence the more concentrated solutions appeared a deeppurple, becoming more and more pink as the d i l u t i o n increased.

The A-c curve for $744 \mu\mu$ shows that A decreases by a large amount with dilution, dropping from 0.128 for $c =$ 0.7 to 0.080 for $c = $ 0.1. This is the only A-c curve which has been plotted for

Fig. 3a

a wave-length lying on the edge of the red-yellow absorption band, for this edge is tremendously sharp compared to the edge of the analogous band of the water solution. The A-c curves for the region of transmission, $764 \mu\mu$ to $920 \mu\mu$, and for the edge of the infra-red band $920 \mu\mu$ to $1134 \mu\mu$, show that A for these regions of the spectrum remains approximately constant for all concentrations.

Cobalt Chloride in Ethyl Alcohol. (*Fig. 4*)

Four solutions were prepared varying in concentration from $c =$ 0.4 to $c =$ 0.1. A month later a second series of more dilute solutions for which c was 0.08, 0.06, 0.05, 0.04, 0.03, 0.02, 0.01, 0.005, were prepared, and their absorption curves

drawn only in the regions of moderate absorption, from $1056\mu\mu$ to $1134\mu\mu$, and for $724\mu\mu$. In the other regions they either absorbed too much, or too little, so that no confidence could be placed in the values of A.
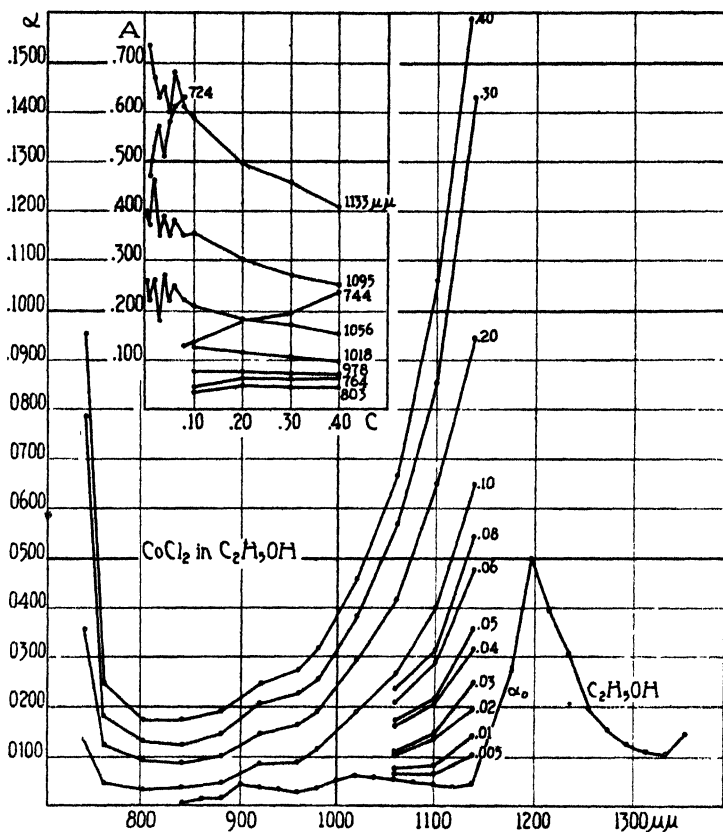
Fig. 4

The absorption curves for the ethyl alcohol solutions are similar in their general character to those for methyl alcohol. The minimum of absorption occurs in the same place, at $842\,\mu\mu$, and the steepness of the edge of the bands is much the same. The ethyl alcohol solutions were of a pure deep blue in the higher concentrations, becoming greenish blue as dilution increased.

The A-*c* curves for $724\mu\mu$ and $744\mu\mu$ show that A decreases with dilution, and the decrease in this case is far greater than in the case of methyl alcohol. For wave-lengths $764\mu\mu$ to $979\mu\mu$ in the region of transmission, A is fairly constant. For the region on the edge of the infra-red band, 1018 to 1134, the A-*c* curves show that A increases with dilution. These last mentioned curves illustrate the magnitude of the error in the determination of A in the case of very dilute solutions.

Cobalt Chloride in Propyl Alcohol. (*Fig. 5*)

Eight solutions were prepared varying in concentration from *c* = 0.434 to *c* = 0.10. The character of the absorption
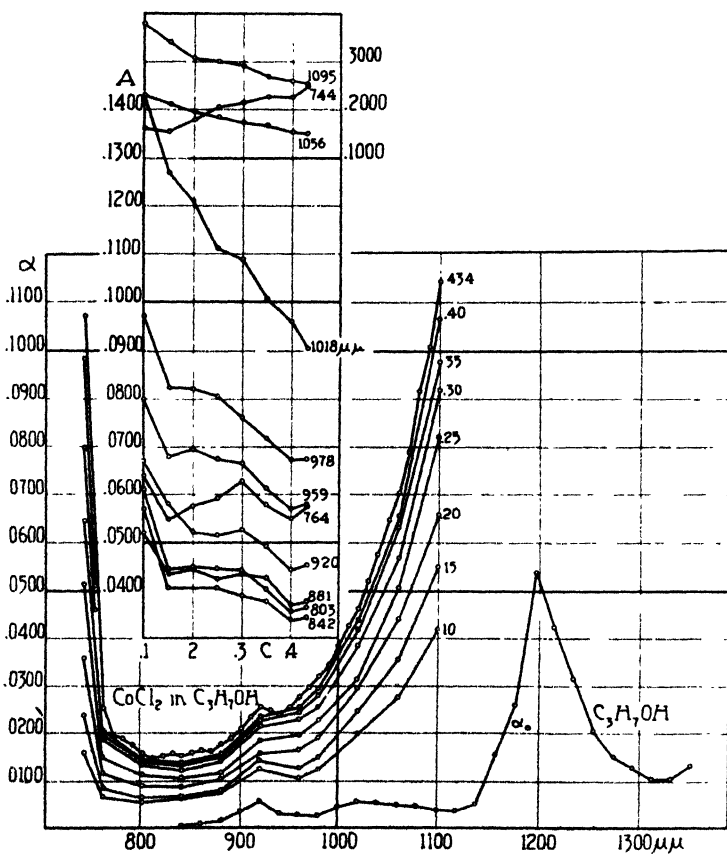
Fig. 5

curves is the same as that of the ethyl alcohol solutions, the minimum of absorption occurring again at 842μμ, and the steepness of the edges of the bands being similar. The propyl alcohol solutions were also deep blue, becoming a greenish blue upon dilution. The absorption curve for c = 0.434 has been drawn in greater detail, readings having been taken at every 10μμ.

The A-c curve for 744μμ, lying on the edge of the yellow-red absorption band, shows A to decrease greatly with dilution. This curve (and the A-c curves for 1056μμ and 1095μμ) have been plotted on a scale of ordinates ten times as small as the other A-c curves. For wave-lengths in the region of low absorption, 764μμ to 842μμ, A is approximately constant, although in this region the values of α are so small that the values of A are liable to considerable inaccuracy. The A-c curves for wave-lengths 920μμ to 1095μμ, on the edge of the infra-red band, show that A increases rapidly with dilution.

Cobalt Chloride in Iso-Butyl Alcohol.   (Fig. 6)

Four solutions were prepared varying in concentration from c = 0.194 to c = 0.05. The absorption curves have the same character as those for the ethyl alcohol solutions, and the color of the solutions in the bottles was the same, being a deep blue which changed to a greenish blue upon dilution. In preparing the solutions the usual precedure was followed, namely, to make the dilutions by addition of the pure alcohol to the saturated mother solution. It was found that a precipitate appeared immediately upon dilution. The solutions were then filtered, and the concentrations measured by a determination of the density. The value of the concentration determined in this way was found to agree within the error of experiment with the concentration calculated from the known amount of dilution. This showed that the loss by precipitation was either negligible, or that the precipitate contained nearly equal parts of cobalt chloride and iso-butyl alcohol. The filtered solutions appeared quite free from any visible particles.

In the cells they had a somewhat cloudy appearance, suggestive of a colloid condition. They showed slightly a Tyndall cone in blue light. An examination of these freshly filtered iso-butyl alcohol (and also the iso-amyl alcohol) solutions with the ultramicroscope showed that they were not colloidal in nature, but that they contained a number of particles. Whether these particles were newly formed precipitate, or some impurity, is unknown.
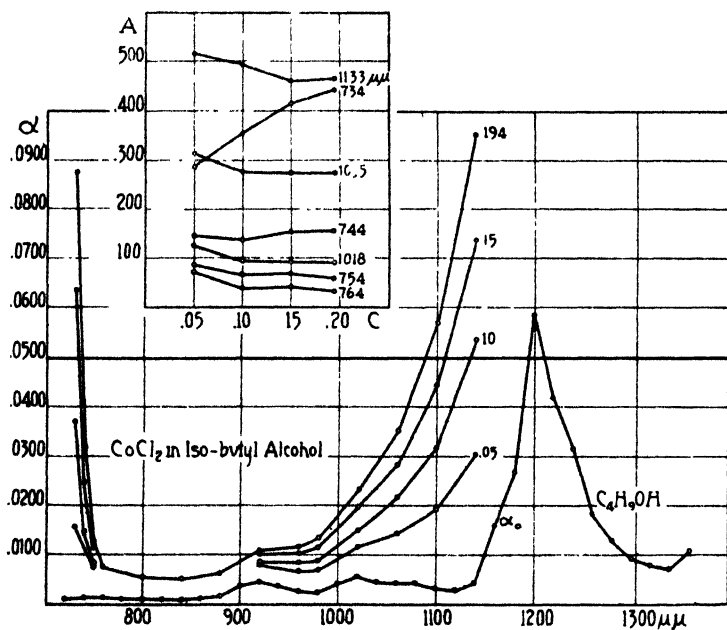
Fig. 6

The A-c curves for $734\mu\mu$ and $744\mu\mu$, wave-lengths lying on the edge of the yellow-red absorption band, show again that A decreases rapidly with dilution. For the wave-lengths $754\mu\mu$ and $764\mu\mu$ in the region of transmission A is a constant. The behavior of the edge of the infra-red band is similar to the case of the propyl alcohol solutions, for A increases with dilution, as shown by the rise in the A-c curves for wave-lengths $1018\mu\mu$ to $1133\mu\mu$.
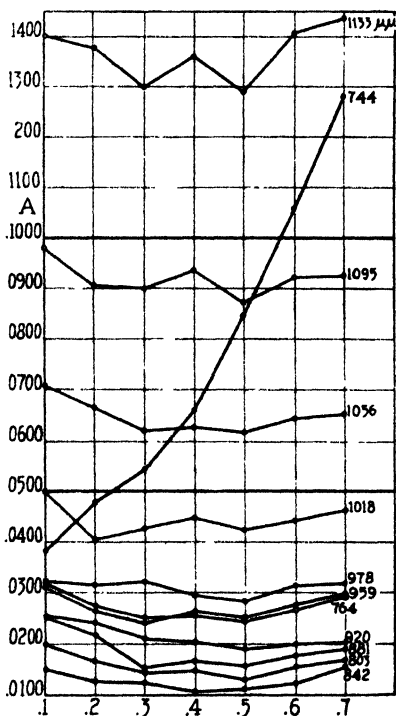
Cobalt Chloride in Iso-amyl Alcohol.   (Fig. 7)

Six solutions were prepared varying in concentration from $c = 0.064$ to $c = 0.010$. The solutions in the bottles were of a deep blue color in the higher concentrations, which changed to a greenish blue upon dilution. The general character of the absorption curves is the same as that of the ethyl alcohol solutions.
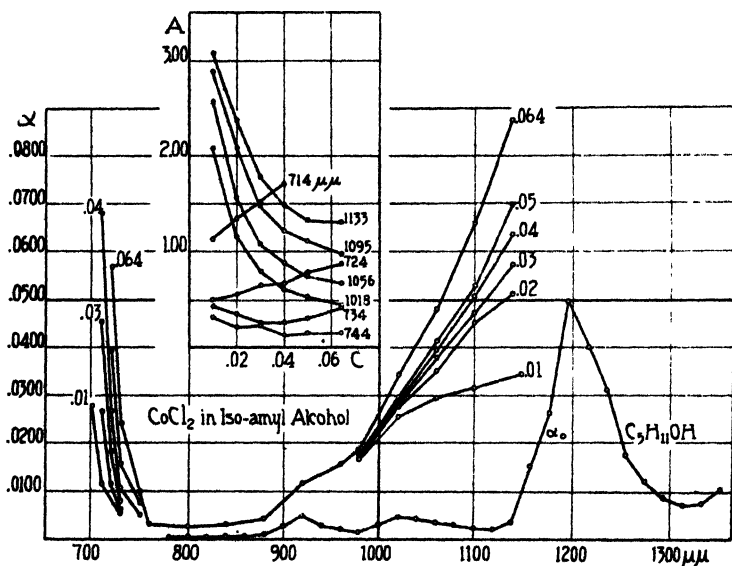
Fig. 7

The iso-amyl alcohol solutions exhibited the same phenomenon of precipitation upon dilution as has been described in the case of the iso-butyl alcohol solutions. They also had the same appearance in the cells, and under the ultramicroscope.

A study was made of the precipitate which was thrown down in these solutions, for the deposit in the case of the iso-amyl alcohol solutions was more abundant than in the case of the deposits in the other cobalt-chloride solutions. The solution was allowed to stand for two weeks, and then the precipitate was filtered off. This precipitate consisted of

blue needle crystals mixed with a flocculent scale-like residue. Analysis showed that in this flocculent residue there was present 54 percent by weight of cobalt chloride. If this precipitate was a compound of the cobalt chloride and the alcohol, this percentage of the chloride would indicate that the compound contained two molecules of the chloride to three of the alcohol.

The A-c curves for the edge of the yellow-red absorption band, at $714\mu\mu$ and $724\mu\mu$, show that A decreases with dilution. In the region of transparency between the two bands A is constant, as shown by the A-c curves for $734\mu\mu$ and $744\mu\mu$. The A-c curves for the edge of the infra-red band show that A increases very rapidly with dilution.

Discussion of Results with Cobalt Chloride

This study of cobalt chloride in water and alcoholic solution brings out the following facts:

In the region of wave-lengths lying on the long wave-length edge of the yellow-red absorption band the A-c curves show that A decreases with dilution. The decrease in A observed in the case of the water solution is considerable, and in the case of the alcoholic solutions this decrease becomes more and more marked as the molecular complexity of the alcohol increases. Jones and Anderson[1] studied solutions of cobalt chloride in water, methyl alcohol, and ethyl alcohol. Plates 2, 4, and 5 of their paper showed that for wave-lengths on the red edge of the yellow-red absorption band A decreased with dilution, and also showed that this decrease was much more marked in the case of the alcoholic solutions than in the water solution. This is in accord with the facts brought out by the measurements discussed in the preceding paragraphs.

In the region of low absorption between the two bands it is concluded that A is constant. As has been mentioned already, in the section concerning cobalt chloride in propyl alcohol, the values of α for the region between the two bands

[1] Carnegie Inst. of Wash., Pub. 110.

are so small that the values of A are in many cases worthless.

In the region of wave-lengths lying on the edge of the infra-red band A experiences deviations from a constant value, and again these deviations show a certain regularity concomitant with the increasing molecular complexity of the solvent. In this region A is nearly constant for the water solutions, but increases with dilution for the alcohol solutions, the increase becoming greater as the molecular weight of the alcohol increases.

Conclusion

The relation between A, the molecular light absorption coefficient of the solution, defined by equation (2), and c, the concentration of the solution in gram-molecules of salt per liter of solution, has been determined. It has been found that in general A is not a constant. In certain cases A decreases with dilution, in other cases A increases with dilution, and in still other cases as dilution proceeds A decreases to a minimum, and then increases again. Another possible combination, namely, that A should increase to a maximum and then decrease, was not met with.

At present there is no adequate theory to explain the facts which have been recorded here. The fact that A varies with c has been probably correctly attributed by Jones and Anderson[1] and others to the formation of complexes, which were considered to be loose chemical compounds of molecules of the salt with molecules of the solvent. Undoubtedly the changes in A with c observed in this investigation may be explained in a qualitative manner by the hypothesis of complexes, or "solvates" as they have been called. But before it can be useful for the interpretation of quantitative data, the solvate hypothesis must be couched in mathematical terms.

The Johns Hopkins University
May 10, 1916

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[1] Loc. cit.

NEW BOOKS

The Metallography of Steel and Cast Iron. *By Henry M. Howe.* *26 x 20 cm;* *pp. xxviii + 641* *New York: McGraw-Hill Book Company, Inc. 1916. Price:* *$10.00.* In the preface the author says: "This volume consists of two distinct parts, an introduction to the new science of microscopic metallography, as applied to steel and to cast iron, and an extended study of the very new branch of that science, the mechanism of plastic deformation. It is through the application of the principles of these subjects that the great advances in the metallurgy of iron and steel are to be expected. The mechanism of deformation has been before us so little that a word as to its importance may not be amiss. The usefulness of steel really results from its resistance to deformation, and its power to endure limited plastic deformation. Hence a knowledge of the mechanism of this deformation and of the way in which steel in part resists deformation and in part accommodates itself to it, may in time disclose to us the essence of its power of resistance and accommodation To understand this essence is to be the better prepared to approach the problem of fitting the metal for its service to our race, not empirically alone but also scientifically."

"Greatly as steel and cast iron differ from each other in manufacture, properties, and application, they form for the metallographist two conterminous divisions of a single series, so closely united that, for the purposes of a general survey, they may well be studied together. Partly on this account, and partly because metallography seems to me to hold out even greater promise to the iron founder than to the steel maker, I have devoted a considerable fraction of this work to the metallography of cast iron. I find strong reason to hope that the intelligent application of metallography may succeed in improving the properties of cast iron to such a degree as to broaden its application greatly. Indeed, a relatively small degree of improvement might well lead to a disproportionate broadening. That so little has been done intelligently to improve the properties of this product by applying metallography to it can be explained in part by the extreme complexity of this branch of the subject, and in part by the usually slighter technical training of the iron founder than of the steel maker. But that so little has been done, far from disproving, tends rather to suggest that much remains to be done, and to add to the attraction of this field, as yet only roughly surveyed."

The subject is treated under the general headings: introduction; thoughts on the permanence of our supply of iron; outline of the classification and manufacture of iron and steel; classification and nomenclature; outline of the constitution of iron; sodium nitrate-water diagram; introduction to the carbon-iron diagram (cementite-austenite or metastable form, the transformation of steel, the transformations in cast iron); graphitization; the phase rule; evidence that the structure of metals is crystalline; general considerations of deformation; specific deformation, slipbands; silhouettes; discussion of slipbands; Beilby's amorphous theory; plastic deformation in steel; twins; the Neumann bands or mechanical twins in ferrite; mechanism of twinning; the X bands; the deformation lines in Hadfield's austenitic manganese steel; is there fluid as well as crystalline motion in metals?; inter-granular and trans-crys-

talline rupture; relative preference of the path of rupture for ferrite and pearlite; fracture; ghosts and the other elements of fiber; influence of manufacturing conditions on fiber; certain crystalline intersections.

On p. 196 the author summarizes the discussion on hardening. "Apart from hardening by cold deformation, which is generally thought to act by amorphizing part of any ductile metal, there are five distinct methods, three of them dynamic and two static, three involving temperature changes and two at stationary temperature, of bringing iron to a hard state intermediate between the soft gamma and the softer alpha states. The hardness of mixtures of this hard state with one or both of the soft end states is so great as to indicate that the hardness of the hard state, if it could be completely isolated, would be some ten times that of alpha iron and far greater than that of gamma.

"I infer that this intermediate state is not amorphous iron, first, because this hardening can be induced statically and thus without mechanism capable of causing amorphism; second, because it endures through long heating at temperatures as high as 800° (method (2)) at which amorphous iron would become crystalline and fine-grained iron would coarsen and thus reduce its amorphous envelopes to a relatively negligible quantity; and third, because the hardness, for instance, of quenched carbon steel, decreases progressively on the slightest heating, whereas that of iron made amorphous by cold deformation increases on gentle heating, so that the hard constituent of such hardened steel differs strikingly from the amorphous hard constituent of cold deformed iron.

"Amorphism as the common cause of hardening by these five methods being thus eliminated, there remain the solution hypothesis that the intermediate hard state is a simple solution in varying proportions of the two end states in each other, the high temperature gamma and the low temperature alpha; and the beta hypothesis that it is a distinct beta state or states of iron, coördinate with the end states gamma and alpha. Gamma iron alone is dense, beta I and II alone are hard, and beta II and alpha alone are magnetic, both gamma and alpha being isolated easily, but beta thus far always occurring mixed with either gamma or alpha or more often both.

"Between these I choose the beta hypothesis confidently, first, because the hardness of the hardened steel is far too great to represent a simple solution of the two soft end states in each other, especially in view of the slight increase of hardness which the dissolving of the glass hard cementite causes in gamma iron, and because this extreme hardness points to the presence of a far harder allotropic variety; second, because the sharpness of the inflection of the curve of the temperature coefficient resistance, and the sharpness of the extinction of magnetism, at or close to A_2, are so marked as to represent an allotropic change here rather than a mere progressive change in the proportions in which alpha and gamma are dissolved in each other; and third, because, for given degree of hardness, the variations in magnetism are far too great to be explained by variations in the proportions of only two substances, gamma and alpha, for such an admixture should, or given hardness, have only one or at most two relatively fixed degrees of magnetism, whereas the beta hypothesis of one hard mixed with one bulky and one or two magnetic substances might give almost any intermediate combination of hardness and magnetism. This third reason is reinforced by the fact that the variations in the ratio of hardness to

magnetism with varying conditions of hardening are those which should be caused by the greater bulkiness of the beta and alpha than of the gamma state.

"Nevertheless, in view of the hardening, slight though it be, of the copper aluminum alloys by quenching from above their transformation range, referable perhaps to the dissolving of the end constituents in each other and perhaps to amorphism caused by the quenching strains, it may be that, in the hardening of carbon steel by quenching, both solution and amorphism may contribute to the resultant hardening, that solution may in all the other hardening methods, and that amorphism may in all the dynamic methods.

"The solution and the amorphous hypotheses, though each fitting some of the facts, yet fail by themselves to explain others. The beta hypothesis thus liberally applied seems to me to fit all the present and intricately related facts, many of them at first sight contradictory, with a degree of accuracy which justifies us in adopting it provisionally with some confidence for working purposes.

"Because the solution of cementite in gamma iron hardens it so little, and because the hardness given by the static methods, which exclude amorphism, is nearly as great as the greatest given by quenching, I infer that the contribution of solution and amorphism to the hardening of steel is of minor importance, and the preservation of much iron in the beta state the dominant cause."

The reviewer believes that it is unfortunate to assume that Fe_3C is a metastable phase under all conditions, p 131. The author adopts Beilby's theory of amorphous films, pp. 373, 381, though he apparently does not concede all that is claimed for it, p. 498. This is a monumental piece of work and the reproductions of the micrographs are astonishingly well done.

Wilder D. Bancroft

The Flotation Process. *By Herbert A. Megraw.* 23 × 16 cm; pp. ix + 249. *New York: McGraw-Hill Book Company, Inc., 1916. Price: $2.50 net.*—In the preface to his book the author makes the following observations:

"The state of the art of concentrating ores by flotation is not such that a text-book can be said to cover the field with any degree of intensiveness The process has not been developed sufficiently to provide a basis for a work that will endure for a great length of time without careful, perhaps radical revision. The theory upon which the process operates has not been fully elucidated, and practice has not been so formulated that much forecasting can be indulged in. The probabilities are that flotation is still in its swaddling clothes and the measure of its full growth cannot be even imagined now. That its usefulness will continue to increase for a long time seems unquestionable."

The book is intended primarily for the engineer and mine-operator and it aims accordingly to give a summary of the status of ore-flotation, particularly as it has been developed in America up to the present. The chapters include a discussion of the patent records, the theory of ore-flotation, oils and their uses, flotation testing, together with numerous detailed descriptions of flotation plants that have been installed in various parts of the world. More than half of the book is taken up by these descriptions.

Several statements appearing here and there interested the reviewer. On page 38 the observation is made that sufficiently fine particles in the pulp will aid in producing a froth, having essentially the same effect as a colloid present

in the oil, which we know aids the formation of air-in-oil foams. The reviewer has noticed this in some experiments of his own, but hitherto has seen no reference to it in any published paper. It is probable that the solid particles re-enforce the oil film surrounding the air bubbles and help the limited quantity of oil present to spread out over the very large air-water interface.

On the same page there are a few interesting remarks on the spreading of "collecting" and "frothing" oils on a water surface. This is a very important point which has been overlooked in the past and careful experiments along this line will undoubtedly produce some valuable results. A foam of value in flotation cannot be obtained unless the oil spreads rapidly and completely. On page 58 the statement is made that oil in excess tends to destroy the froth. This is interesting in view of the fact that Hardy once observed a maximum frothing action on blowing air through water on the surface of which was spread an extremely thin film of oil. On adding more oil the frothing diminished rapidly. It all goes back to the peculiar behavior of oil films on water, a problem that we have got to straighten out before we can hope to understand all that happens in the flotation mill.

The book as a whole is a useful one. The chapter on flotation oils is written in a distinctly haphazard fashion and statements are repeated in some cases within two or three pages. However, the author is to be congratulated for not having called upon surface tension to do the many extraordinary things that we have had attributed to it in recent publications. *T. R. Briggs*

General Chemistry. *By 'Hamilton P. Cady. 21 × 15 cm; pp xiv + 522. New York: McGraw-Hill Book Company, Inc., 1916. Price: $2.25 net.*—This book is a condensed and simplified form of the author's inorganic chemistry (**17,** 369). The general arrangement is much the same; the most marked difference from the earlier book is to be found in the treatment of the atomic theory. "The author feels that the recent advances have justified a more unqualified support of this theory than was accorded in the former work. By introducing an experimental conception of molar weights before taking up the chapter on atomic weights, the author feels that he has been able to develop the conception of atomic weights in a very simple manner from the experimental standpoint. The theory is then brought in as an explanation for the facts previously discussed."

The headings of the chapters are: introduction; units; oxygen; hydrogen; water, combining weights and atomic theory; hydrogen peroxide; chlorine; ionic theory; oxygen compounds of chlorine; bromine, iodine, and fluorine; sulfur; selenium and tellurium; nitrogen, phosphorus; carbon; silicon; boron; the argon group; the metallic elements; the alkali metals; the metals of the alkaline earths; the magnesium sub-group; copper, silver, and gold; group III; group IV; group V; group VI; group VII; group VIII; radio-activity.

As an illustration of the difficulty in avoiding mistakes, one may cite the diagram of the Townsend cell, p. 281, which does not agree with the text and which apparently escaped notice for four years in the earlier book.

Wilder D. Bancroft

INVESTIGATIONS UPON ABNORMAL ELECTRO-
LYTIC DISSOCIATION

BY A. N. SAKHANOV

1. Investigations upon Conductivity

Investigations of the present day have shown to us that in many non-aqueous solutions the molecular conductivity of electrolytes decreases with increasing dilution. This phenomenon, which is known under the name of abnormal dissociation, obeys the following empirical laws:[1]

1. The equation, connecting the molecular conductivity with dilution, is expressed in the following way:

$$\lambda_v{}^n = \text{const.},$$

where λ stands for the molecular conductivity, v for dilution and n is a constant.

2. Abnormal dissociation is a property common to all the solvents with low dielectric constants.

3. The decrease of the molecular conductivity with increasing dilution takes place sooner for a given electrolyte, the smaller the dielectric constant of the solvent.

4. At a definite dilution the molecular conductivity reaches a minimum and then increases normally with further dilution.

5. A maximum of molecular conductivity is found in highly concentrated solutions.

The purpose of our investigation is not only to treat the question of abnormal electrolytic dissociation in solvents with high dielectric constants, but also to explain the causes of that phenomenon. In order to test the first statement we have used silver nitrate as an electrolyte.[2] The following substances have been taken as solvents: aniline, quinoline, pyridine, metachloraniline, acetonitrile, water, and also some mixtures of the above-mentioned substances have been used. The dielectric constants of the mixtures were estimated from

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[1] For more details see my article in Zeit. Elektrochemie, 20, 529 (1914).

[2] These investigations were carried out with Messrs. Prscheborovsky and Rabinovitch.

Bouty[1] and Silberstein's[2] equations, the average values being taken. Thus we have obtained the following thoroughly studied solvents:

Solvents	Diel. const.
Aniline	6.85
Mixture: 4 vol. of aniline + 1 vol. of pyridine	8.0
Quinoline	8.9
Mixture: 1 vol. of aniline + 1 vol. of pyridine	9.7
Pyridine	12.56
Meta-chloraniline	13.35
Mixture: 2 vol. of pyridine + 1 vol. of acetonitrile	19.7
Acetonitrile	36.1
Mixture: 1 vol. of acetonitrile + 1 vol. of water	59.7
Water	81.7

Special care has been taken as to the purity of the substances. Aniline and quinoline were obtained from Kahlbaum (mark "Kahlbaum"). After being dried thoroughly by means of potassium hydroxide, they were distilled. Pyridine was also obtained from pyridine "Kahlbaum," after being boiled for a long time with a reflux condenser in the presence of potassium hydroxide. Acetonitrile was prepared by distillation of Kahlbaum's product in the presence of phosphorus pentoxide.

The conductivity of silver nitrate in aniline and quinoline had been determined before.[3] My data for aniline agree closely with Pearce's[4] recent data but those for quinoline are somewhat different from Pearce's. The character of the curve of the molecular conductivity is the same, however. On the contrary, Pearce's conductivity data for silver nitrate in pyridine not only differ greatly from mine, but also show differences in the very character of the curve itself. Dutoit and Friderich[5] have investigated dilute solutions of silver nitrate

[1] Comptes rendus. 114, 1421 (1892).

[2] Wied. Ann., 56, 661 (1895).

[3] Jour. Russ. Chem. Soc., 42, 683 (1910); Zeit. phys. Chem., 83, 129 (1913).

[4] Jour. Phys. Chem., 19, 12 (1915).

[5] Bull. Soc. chim. Paris, (3) 19, 321 (1899).

in acetonitrile and their results coincide with ours. The difference between our results for silver nitrate in pyridine and those of Pearce's is due perhaps to the difficulty which arises in obtaining absolutely identical samples. Similar and even still greater deviations often take place in the case of boiling-point determinations, viscosity measurements, etc.

As may be seen from the tables, we have also studied highly concentrated solutions. The viscosity of such solutions differs greatly from that of the pure solvent and of dilute solutions. In order to compare the conductivities of concentrated solutions with each other, as well as with those of dilute solutions, it is necessary to correct for this and to express the results in terms of the viscosity of the pure solvent.

A number of investigators[1] have found that the ion-velocity is either proportional to the viscosity of the medium or the viscosity raised to a certain power. The latter must approximate unity. Therefore, the values of conductivities for solutions with higher concentrations are corrected after either of the following equations:

$$L = \lambda . \frac{\eta}{\eta_0} \text{ or } L = \lambda . \left(\frac{\eta}{\eta_0}\right)^m$$

where L denotes the corrected molecular conductivity, λ the directly measured molecular conductivity, η and η_0 are viscosity coefficients of the solution and the pure solvent, respectively.

We have corrected the values of the molecular conductivities after the simplest of the equations, the reason for this being that in the second equation the exponents are approximating unity and because the minimum of corrected molecular conductivity is obtained at the comparatively low value of the ratio η/η_0 where both equations give similar L-values. The values for the corrected molecular conductivity from the two equations differ greatly from each other only in the case of the highly concentrated solutions, where the value of the

[1] Kohlrausch: Proc. Roy. Soc., **71**, 338 (1903); Walden: Zeit. phys. Chem., **55**, 207 (1906); Johnston: Jour. Am. Chem. Soc., **31**, 1010 (1909); Washburn: Ibid., **33**, 1469 (1911).

ratio η/η_o is too great. As the problem of the present investigation is to find minima of molecular conductivity, therefore, the real values of the corrected molecular conductivity for highly concentrated solutions are of little importance for us.

The following Table I contains the results of our measurements (in recipr. ohm) at $25°$ ± $0.05°$.

TABLE I

Conductivity and Viscosity of Solutions

I. Silver Nitrate in Aniline

Dilution in lit. v	Mol. conduct. λ	Ratio[1] $\eta : \eta_o$	Corr. mol. cond. L
186.6	0.37	1.00	0.37
112.9	0.33	1.00	0.33
52.4	0.32 (Minim.)	1.02	0.33 (Minim.)
32.6	0.34	1.03	0.35
26.38	0.36	1.04	0 37
18.35	0.39	1.06	0.41
10.41	0.64	1.10	0.70
6.76	0.85	1.19	1.01
3.24	1.54	1.46	2.25
1.560	1.96 (Maxim.)	2.33	4.57
0.911	1.57	—	—
0.570	0.76	—	—
0.543	0.62	—	—

II. Silver nitrate in mixture: 4 vol. of aniline + 1 vol. of pyridine

v	λ	$\eta : \eta_o$	L
253.4	4.39	1.00	4.39
61.3	3.77	1.02	3.85
47.9	3.72 (Minim.)	1.02	3.79 (Minim.)
27.3	3.81	1.04	3.96
15.6	4.13	1.07	4.42
7.52	4.89	1.16	5.67
3.58	5.53 (Maxim.)	1.40	7.35
1.712	4.96	2.05	10.2
0.774	2.47	5.3	13.0

[1] For absolute data of viscosity see Jour. Russ. Chem. Soc., **47**, 849 (1915).

III. Silver nitrate in quinoline.

v	λ	η : η₀	L
92.65	3.05	1.01	3.08
35.73	2.73	1.03	2.81 (Minim.)
13.51	2.61	1.11	2.90
7.17	2.62 (bending)	1.24	3 17
4.78	2.56	1 41	3.61
3.48	2.37	1.64	3.89
2.404	2.08	2.08	4.33

IV. Silver nitrate in mixture: 1 vol. of aniline + 1 vol. of pyridine

v	λ	η : η₀	L
220.4	14.86	1.00	14.9
62.10	11.76	1.01	11.9
35.85	11.06	1 03	11.4
16.09	10.79	1.06	11.4 (Minim.)
8.37	10.92 (bending)	1 13	12.3
3.83	10.94	1.34	14.7
1.736	9.26	1.92	17.8
0.804	5.15	4.38	22.6
0.431	1.365	20.8	28.4

V. Silver nitrate in pyridine

v	λ	η : η₀	L
175.7	41.6	1.00	41 6
89.26	36.6	1.00	36.6
57.10	33.8	1.00	33.8
23.56	30.0	1.02	30.6
15.46	28.7	1.05	30.1 (Minim.)
6.37	26.7	1.14	30.4
3.98	25.2	1.22	30.7
2.04	22.3	1.44	32.1
1.250	18.2	1.92	34.9
0.945	15.6	2.48	38.7
0.572	8.9	4.96	44.1

VI. Silver nitrate in meta-chloraniline

v	λ	$\eta : \eta_0$	L
176.8	1.57	1.007	1.58
75.26	1.12	1.02	1.14
27.54	0.805	1.05	0.84
11.80	0.694	1.12	0.78 (Minim.)
4.42	0.683	1.38	0.95
1.660	0.605	2.63	1.59

VII. Silver nitrate in mixture: 2 vol. of pyridine + 1 vol. of acetonitrile

v	λ	$\eta : \eta_0$	L
263.8	85.1	1.00	85.1
18.02	61.2	1.02	62.5
13.30	57.6	1.03	59.4
5.55	48.3	1.10	53.1
2.27	36.7	1.29	47.3 (Minim.)
1.866	33.2	1.43	47.5
0.964	24.0	2.19	50.2
0.473	10.3	5.16	53.0

VIII. Silver nitrate in acetonitrile

v	λ	$\eta : \eta_0$	L
61.8	113.0	1.0	113.0
31.9	93.6	1.0	93.6
8.70	61.25	1.10	67.4
3.73	44.20	1.17	51.7
1.630	31.80	1.40	44.5
1.076	26.00	1.60	41.6 (Minim.)
0.593	19.30	2.3	44.4
0.359	13.70	4.6	63.0
0.294	11.50	6.2	71.0
0.194	6.56	18.0	118.0

IX. Silver nitrate in mixture: 1 vol. of acetonitrile + 1 vol. of water

v	λ	$\eta : \eta_0$	L
46.93	98.2	1.0	98.2
13.25	89.7	1.0	89.7
7.70	84.7	1.02	85.0
3.511	76.9	1.07	82.4
1.644	65.6	1.23	80.7
0.883	53 1	1.48	78.5 (Minim.)
0.547	42.3	1.87	78.9
0.370	32.7	2.45	80.2
0.203	20 5	3.93	80.6
0.1149	12.36	7.24	89.6

X. Silver nitrate in water

v	λ	$\eta : \eta_0$	L
0.7128	71.27	1.11	79.11
0.3587	56 88	1.27	72.24
0.2061	43.84	1.63	71.46 (Minim.)
0.1182	20.52	2.74	80.88

The results obtained show how important for the right characterization of electrolytic dissociation are the corrections for the change of viscosity. It is only in solvents with di-electric constants not over 8.0 that the curve of molecular conductivity for silver nitrate reveals rather sharply the phenomenon of abnormal dissociation with the formation of a minimum and maximum (Solvents I and II). In solvents with dielectric constants between 8.5–10.0 the curve of molecu-lar conductivity (λ) forms only bendings (Solvents II and IV). And finally in solvents with dielectric constants over 10 the molecular conductivity increases continually with the dilution. If, however, the conductivity values be corrected for the changed viscosity, the curve of corrected molecular conduc-tivity for silver nitrate shows distinctly marked minima in all solvents. *Thus in solvents with dielectric constants over 10 the continual increase of molecular conductivity (λ) with dilution depends upon the great increase of viscosity of the solu-tions with increasing concentration.*

The position of the minima of corrected molecular con-

ductivity depends strictly upon the dielectric constant of the solvent; that is, *with the increase of dielectric constant minima are gradually displaced to the region of more and more concentrated solutions.* For this reason in the case of aniline the minimum occurs at a comparatively high dilution. In solvents with still lower dielectric constants, such as amylamine, or benzylamine, minima of molecular conductance for silver nitrate were not noticed, the reason being, of course, because they lie in higher dilutions, where the conductivity of the solutions is too slight. However, in the case of such solvents as water, minima can be detected only with difficulty for just the opposite reason, because they lie in the region of highly concentrated solutions.

Walden[1] showed that there exists a certain relation between the position of the minimum of molecular conductivity (dilution $= V_m$) and the dielectric constant (D) of the solvent:

$$D.\sqrt[3]{V_m} = \text{const.}$$

Nevertheless he proved that this equation can be applied only to solvents with small dielectric constants, since the values of the molecular conductivity were not corrected for the changed viscosity.

The following Table II contains the results obtained concerning the position of minima of corrected molecular conductivity for silver nitrate.

As may be seen from the table, Walden's equation can be applied perfectly to solvents with dielectric constants up to 35. It is rather important to note that *the constancy of the product $D\sqrt[3]{V_m}$ occurs only when the corrected molecular conductivities (L) are used.*

For solvents with dielectric constants over 35 the product $(D\sqrt[3]{V_m})$ increases. The reason for this phenomenon may be that there are real deviations from Walden's equation in the case of solvents with rather high dielectric constants. However, we must not forget that the correction of conductivities made by means of the above-mentioned equation was only ap-

[1] Bull. Akad. Sci. Petersb., **1913,** 1083.

<div align="center">TABLE II</div>

Solvent	Diel. const.	Dilution	$D\sqrt[3]{V_m}$
Aniline	6.85	60 Lit	29 5
Mixture: 4 vol. of aniline + 1 vol. of pyridine	8.0	50 Lit	29.5
Quinoline	8 9	45 Lit	31.7
Mixture: 1 vol. of aniline + 1 vol of pyridine	9.7	35 Lit	31.7
Pyridine	12 56	15 Lit	31.0
Mixture: 2 vol. of pyridine + 1 vol. of acetonitrile	19.7	3 Lit	28.4
Metachloraniline	13.35	12 Lit	30.6
Acetonitrile	35.8	1 Lit	35 8
Mixture: 1 vol. of acetonitrile + 1 vol. of water	59.7	0 7 Lit	53.0
Water	81.7	0.2 Lit	47.4

proximative, especially for highly concentrated solutions, where minima are found for such solvents as water. The conductivity values corrected by means of the equation are too high for concentrated solutions and the real minima also must lie in the region of more concentrated solutions. Therefore, the values of V_m for the last two solvents, IX and X, are smaller than those given in the table and the application of the Walden equation to the last two solvents is not excluded.

A perfectly regular displacement of minima of corrected molecular conductivity with the increase of the dielectric constant of the solvent forces us to draw a conclusion that at some concentration or other for each of the above-tested solvents there is found the phenomenon of abnormal dissociation, upon which depends both the formation of minima and the further increase of molecular conductivity with the concentration.

This conclusion holds true for the solvents with dielectric constants up to 36. Nevertheless for the last two solvents, IX and X, extrapolation is necessary as in these cases the abnormal dissociation can be found only in the region of highly concentrated solutions. Bowden's[1] investigation of this ques-

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[1] Jour. Chem. Soc., **99**, 194 (1911); McBain and Taylor: Zeit. phys. Chem., **76**, 179 (1911); Bunbury and Martin: Jour. Chem. Soc., **105**, 417 (1914).

tion as well as investigations of others have not only removed all doubts concerning this question, but have also proved that some electrolytes in aqueous solutions form minima of molecular conductivity at comparatively low concentrations and without any corrections for changed viscosity.

Thus we draw the following very important conclusions: The *corrected molecular conductivity (L) of silver nitrate forms minima in all the solvents studied with dielectric constants between 6–82 and the position of these minima is determined by the dielectric constant. The abnormal dissociation decreases with the increase of the dielectric constant of solvent. Therefore, only for solvents with low dielectric constants is the abnormal dissociation a very characteristic property.*

The phenomenon of electrolytic dissociation is determined by the action of two factors. Ion formation proceeds by means of normal as well as abnormal dissociation.

The corrected molecular conductivity, having passed through the minimum, increases continually with the concentration. This is shown clearly by measurements in which we have reached, at least in some cases, exceedingly high concentration of salt.

This phenomenon in its turn leads to the following very important conclusion: *the curve of the corrected molecular conductivities intersects the axis of the ordinates (the dilution being = O) at a certain positive value of the ordinate.*

In the Solvents I and II the directly measured molecular conductivity (λ) forms distinctly marked maxima. In the Solvents III and IV bendings are formed, *i. e.*, faintly marked and brought together maxima and minima. In Solvents V–X, with still higher dielectric constants there are already neither maxima nor bendings. Thus we arrive at the conclusion that *maxima of molecular conductivity (λ) are formed in solvents with dielectric constants up to 10.*

All these conclusions are drawn as the result of the investigation of one electrolyte, silver nitrate, but unquestionably they can be applied as well to other "normal" electrolytes of the silver nitrate type: salts of ammonium, tetraethylam-

monium, etc. At the same time they hold true only for so-called "normal" electrolytes.

2. Investigations upon the Transport-Numbers

Notwithstanding the fact that the most important laws, governing the abnormal electrolytic dissociation, are fixed experimentally, up to the present day we have not any universally accepted hypothesis or theory concerning the nature of this phenomenon. In 1905–1906, Steele, McIntosh and Archibald suggested a hypothesis, the essential point of which was that they assumed that in some solvents only the associated molecules of salt are capable of electrolytic dissociation. In 1912–1913, I developed this hypothesis further. The essential point of this hypothesis that associated molecules are more capable of electrolytic dissociation than simpler ones, I have explained from the point of view of Abegg and Bödlander's theory, according to which the electro-affinity of complex ions is greater than that of simple ones.

Anyhow, the principal point of the hypothesis of conducting current complexes is in the firmly fixed phenomenon of polymerization of electrolytes in solvents with small dielectric constants. Likewise the increase of polymerization is always accompanied by the increase of molecular conductivity with concentration: determinations of molecular weights in solvents with low dielectric constants show that in these solvents the salts are associated and that the association increases with the concentration. Therefore, we see the close relation between the two phenomena of abnormal dissociation and of polymerization of the salt.

If an electrolyte is polymerized, the result of its electrolytic dissociation is, as is known, the complex ion. Therefore, the complex ion formation is looked upon as being natural for solvents with low dielectric constants.

Kraus and Bray found that the transport numbers for different salts in liquid ammonia contradict the hypothesis of current conducting complexes. As the transport-numbers for most salts in this solvent change but little with dilution,

therefore, the above-mentioned authors conclude that complex ions are not formed in liquid ammonia. Bringing this conclusion to a general form, the authors consider the complex ion formation as being an exceptional phenomenon.

Anyhow, the absence of change or, more properly speaking, the slight change of transport numbers for many electrolytes in liquid ammonia must be noticed. The fact is that Franklin and Kraus's ebullioscopic measurements in liquid ammonia show that electrolytes in this solvent are polymerized. Since the complex ion formation comes as a result of the electrolytic dissociation of associated molecules, therefore, the presence of complex ions in liquid ammonia is more than probable. If, notwithstanding this, the transport-numbers do not give any hint as to the presence of complex ions, there is, therefore, a contradiction between the ebullioscopic data and those of the transport-numbers.

The second example of similar contradiction we find in Serkov's researches.[1] These investigations, carried out after the method of transport-numbers, show that the complexity of lithium chloride in acetone is greater than that of lithium iodide, in spite of the fact that according to numerous cryoscopic and ebullioscopic measurements iodide salts reveal a greater tendency to form complexes than bromide and especially chloride salts. Thus we perceive here also a difference between the results of the two methods.

These contradictions as well as the chance to come to the question of the cause of abnormal dissociation were the reasons for the following investigation. For this purpose we have measured[2] the transport-number for silver nitrate in aniline and two mixtures of aniline with pyridine (II and IV).

On the other hand, Schlundt[3] has measured the transport-number for the same salt in pyridine and acetonitrile. If to these data be joined Hittorf's data for silver nitrate in aqueous solutions, we shall obtain representation of the change of

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[1] Zeit. phys. Chem., **73,** 500 (1910).
[2] These investigations were carried out by Mr. Grinbaum.
[3] Jour. Phys. Chem., **6,** 159 (1902).

transport-numbers for silver nitrate, depending both upon the concentration of solution as well as upon the dielectric constant of the solvent.

The apparatus, in which the electrolysis took place, was constructed like that of Nernst and Loeb. The anode consisted of a bent silver rod and the cathode of a silver plate. Electrolysis lasted for 3–5 hours. The current strength was from 4 to 8 milliamperes. After the electrolysis was finished the liquid from the apparatus was poured off into weighed bottles through the tap, which was in the lower part of the long tube, where was the anode. Therefore, the first bottle contained the anode layer. Afterwards in the same manner were taken away the two small middle layers. The difference between the whole weight of the liquid in the apparatus and the sum of the anode layer and two middle layers represented the weight of the cathode layer.

The content of the coulometer, as well as the solutions of the layers, were titrated according to Volhard's method with nearly $N/40$ solution of ammonium rhodanate. The titre of that solution was determined before each experiment.

When we have titrated the cathode and anode layers, we have taken only a part of it in order not to add too great a quantity of ammonium rhodanate solution. By adding a sufficient amount of dilute nitric acid we have dissolved the aniline and pyridine of the solutions in the state of nitrate salts. After that the solution thus obtained was diluted with water and was titrated according to Volhard in the presence of ferrous alum.

Different experiments proved that such titration is possible in the presence of aniline nitrate, in case the titration is made sufficiently rapidly. On standing, the solution gradually becomes green because of the reaction between the ferrous salt and aniline nitrate. This very slight greenish or bluish tint, which appears in the diluted solutions a few minutes after the addition of alum, interferes with the titration. The intensity of the color increases with the time. Therefore, we were obliged to make two titrations for each

solution and in the second titration alum was added at the very end of the titration. It must be stated that, after some practice, the first titration, when alum is added at the beginning, was accomplished so quickly that it coincided entirely with the second. The difference between the two titrations rarely reached 0.05 cc.

The middle layers show that the concentration of silver nitrate does not change during the electrolysis in all the experiments included in Table III. Only in two cases have we found that the concentration of the middle layers had changed, evidently in consequence of their being mixed either with the anode or with the cathode solutions. For this reason these two experiments were omitted as being evidently faulty.

The whole quantity of silver nitrate in all the layers, being compared with the quantity before electrolysis took place, was found to be unchanged within the limit of ± 1.5 mg.

As we have determined both the increase of silver at the anode and the decrease of it at the cathode, therefore, in every experiment we have obtained two values for the transport-number: at the anode and at the cathode. The maximum difference between these two values is, as may be seen, 3 percent. The result is quite satisfactory, if we take into consideration that even in aqueous solutions the difference is the same.

The character of the silver deposited on the cathode depends upon the concentration of the solution. In highly concentrated solutions the silver is deposited in the form of a very dense layer. In more dilute solutions the silver is deposited in the form of dendrites or of a black powder sometimes very friable and easily broken off from the cathode. The solutions of silver nitrate at the anode and cathode did not change color during the electrolysis. Only in the very dilute solutions did the cathode solution grow quite yellow during the electrolysis. Evidently the pulverulent silver accelerates catalytically the oxidation of the aniline. When the yellow cathode solutions were treated in dilute nitric acid,

tinted solutions were obtained which were titrated with some difficulty. Therefore, in the case of dilute solutions the transport-number was determined only with the anode solution.

The experiments were carried out at the room temperature, say, at 18°. The results of the experiments are given in Table III.

TABLE III

Time of electrolysis	Current strength	Dilution in liters	Transport-number	
			at anode	at cathode
Solvent: mixture 1 vol. of pyridine + 1 vol. of aniline				
4 hrs. 30 min.	Ca 8	1.40	0.342	0 335
4 hrs. 10 min.	8	4.0	0.353	0 363
4 hrs.	8	10.0	0.372	0.374
4 hrs. 30 min.	6	25.2	0.403	—
Solvent: mixture 1 vol. of pyridine + 4 vol. of aniline				
5 hrs.	8	1.60	0 326	0.329
5 hrs.	8	2 10	0.336	0 337
5 hrs.	7	10.35	0.352	—
3 hrs.	6	19.6	0.395	—
Solvent: aniline				
4 hrs.	8	1.40	0 377	0.369
3 hrs. 7 min.	8	2.20	0.368	0 364
5 hrs. 2 min.	5	5.20	0.345	0.343

As may be seen from the table, the transport-numbers of silver for silver nitrate are considerably smaller for the solvents tested than for water. The transport-number for both mixed solvents decreases with increasing concentration of the salt. On the contrary in pure aniline, as far as the investigated concentrations are considered, we have the reverse phenomenon: the transport-number increases with concentration. Unfortunately because of very high resistance, it was impossible to determine the transport-numbers for solutions more dilute than $N/5$ of silver nitrate in aniline.

It is exceedingly interesting to compare our data with those which Hittorf and Schlundt obtained for the same salt in other solvents. This is dóne in Table IV, where the trans-

port-numbers which we obtained are expressed as average of the measurements for the anode and cathode solutions.

TABLE IV

The transport-numbers of silver for silver nitrate (multiplied by 100)

Solvent dilution:	0.4	1.0	1.5	2	4	5	10	20	25	40
Water	53.2	50.0	—	48.3	47.3	—	—	—	—	47.5
Acetonitrile	—	38.3	—	—	42.2	—	44.8	—	—	47.3
Pyridine	—	32.6	—	34.2	—	—	39.0	—	—	44.0
Mixture: 1 vol. of pyridine + 1 vol. of aniline	—	—	33.8	—	35.8	—	37.3	—	40.3	—
Mixture: 1 vol. of pyridine + 4 vol. of aniline	—	—	32.7	33.6	—	—	35.2	39.5	—	—
Aniline	—	—	37.3	36.6	—	34.4	—	—	—	—

It is seen from Table IV that a decrease of transport-number with increasing concentration takes place in acetonitrile, pyridine and two mixtures. In water and aniline we observe the reverse phenomenon.

All the solvents enumerated in the table (with the exception of aniline for investigated concentration of the salt) demonstrate well the general law: *the transport-numbers for the given electrolyte in dilute solutions do not depend upon the nature of the solvent.* In fact, the more dilute the solutions, the more closely the transport-numbers of silver approach the value of 0.47.

The considerable and regular change of the transport-numbers with dilution was explained by Hittorf and there is hardly anything to be said against this ordinary interpretation. Carrara,[1] Abegg and Neustadt,[2] Schlundt[3] and others likewise admit that the transport-numbers change because of the presence of complex ions—be it cation or anion according to the sign of these changes.

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[1] Elektrochemie nichtwässeriger Lösungen, 25 (1908).

[2] Zeit. phys. Chem., 69, 486 (1910).

[3] Jour. Phys. Chem., 6, 159 (1902).

The considerable and regular decrease of the transport-number of silver with increasing concentration in acetonitrile, pyridine, and two mixtures is due to the fact that the negative electricity is being conducted not only by the ions NO_3', but also by the complex ions evidently of the composition —$Ag(NO_3)_2'$. The concentration of the complex ions increases with concentration of the solution according to the mass law.

It may be seen from Table IV that the normal value of the transport-number of silver (for silver nitrate), 0.47, is obtained at different dilutions, which depend on the dielectric constant of the solvent. This result is a consequence of the theory of complex ions, since the dielectric constant determines the dilution, at which the electrolyte is already to a great extent changed into normal molecules. This explanation of the change of the transport-number is in perfect harmony with the measurements of the molecular weights of silver nitrate in pyridine and aniline. Walden and Centnerschwer,[1] and Walden[2] show that silver nitrate is polymerized in these solvents and that the degree of polymerization increases with the concentration. If silver nitrate is polymerized in both pyridine and aniline it is doubtlessly polymerized in the mixtures of these two solvents.

Quite unexpectedly the transport-number of silver (for silver nitrate) in aniline (as far as the tested concentrations are concerned) changes exactly as in water; that is, increases with the concentration. Moreover the values of the transport-numbers (in tested concentrations) are greater in aniline than in the mixtures. Since silver nitrate is polymerized in aniline, the increase of the transport-number of silver with concentration must be explained by the formation of a complex cation —$Ag_2NO_3^{.}$. From the formation of complex anions in the mixtures of pyridine with aniline we may also decide that such anions are present also in aniline. Drawing a converse conclusion (from the formation of complex cations in

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[1] Zeit. phys. Chem., **55,** 321 (1906).
[2] Bull. Acad. Sci. Petersb. **1913,** 1083.

aniline) we see that the complex cations $Ag_2NO_3^{\cdot}$ are also formed in the mixtures of pyridine with aniline.

Thus *as a general case electrolytic dissociation of associated molecules gives complex anions as well as cations.* For example, the electrolytic dissociation of silver nitrate in any of the solvents leads as a general case to the following processes:

$$AgNO_3 \rightleftharpoons Ag^{\cdot} + NO_3'$$
$$(AgNO_3)_2 \rightleftharpoons Ag^{\cdot} + Ag(NO_3)_2'$$
$$(AgNO_3)_2 \rightleftharpoons Ag_2NO_3^{\cdot} + NO_3'$$
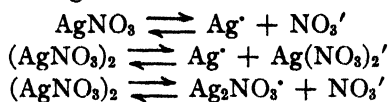
These phenomena may be complicated on the one hand by solvation and on the other hand by the formation of still more highly polymerized molecules than double, as is the case with solutions in chloroform.

Probably the simultaneous formation of complex anions and cations is a frequent phenomenon in non-aqueous solutions. In that case this phenomenon throws light not only on the measurements described in this paper, but also on those contradictions between the data of transport-numbers and the determinations of molecular weights, which we have been speaking of at the beginning of the chapter.

Evidently when the formation of only one complex ion (anion or cation) takes place, the transport-numbers will change abruptly with dilution. Simultaneous formation of both complex ions makes this abrupt change of transport-numbers less marked. If both complex ions are formed in the same quantity, the transport-numbers will be independent of the dilution. Thus in this case the phenomenon will follow exactly as in the case when the formation of complex ions does not occur. In such conditions the method of transport-numbers does not enable us to detect the existence of complex ions. Therefore, when deciding the question of complex ions, the method of transport-numbers must by all means be combined with determinations of molecular weights by cryoscopic or ebullioscopic method.

The slight change of transport-number with dilution in liquid ammonia in connection with determinations of molecular weights can be explained by formation of complex anions and

cations. Likewise the greater change of transport-number of lithium for lithium chloride in acetone, than for lithium iodide can be explained by the fact that lithium iodide, being more polymerized, dissociates so that both ions are in the complex form.

Thus our investigations carried out with the transport-number are in complete harmony with the hypothesis under consideration.

3. Investigations upon the Electromotive Force of Concentration Cells

Because the question of abnormal dissociation is considered to be of great importance, electrometric measurements of concentration cells were made, for example:

$$\overset{+}{Ag} \mid \text{0.1 } N \text{ AgNO}_3 \mid \text{0.001 } N \text{ AgNO}_3 \mid \overset{-}{Ag}$$
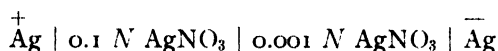
We are giving in the present paper the data only for solutions in pyridine. All the measurements were carried out at a temperature of 25.0 ± 0.05°. The method of measuring is that of Poggendorff and the results are given in the following Table V.

TABLE V.

Electromotive force of concentration cells in pyridine

Solution of AgNO₃ (conc.₁)	Solution of AgNO₃ (conc.₂)	Electromotive force
2 N	0.2 N	0.054 Volt
1.5 N	0.15 N	0.042
1.0 N	0.1 N	0.035
1.0 N	0.01 N	0.070
1.0 N	0.001 N	0.114
0.2 N	0.01 N	0.050
0.1 N	0.01 N	0.038
0.1 N	0.001 N	0.080
0.01 N	0.001 N	0.041
0.001 N	0.0001 N	0.053

As may be seen from the table, in very dilute solutions in pyridine the electromotive force of concentration cells

approaches the normal value. For example, the electromotive force of the cell

$$\text{Ag} \mid \text{0.001 } N \text{ AgNO}_3 \mid \text{0.0001 } N \text{ AgNO}_3 \mid \text{Ag}$$
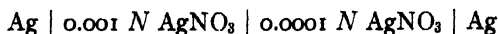
in pyridine is equal to 0.053 volt, whereas that for the corresponding cell in aqueous solution is 0.055 volt. This fact proves that *Nernst's theory can be applied to solutions in pyridine.* On this basis we calculate the ion concentration and the degree of dissociation of silver nitrate in pyridine after Nernst's simplest equation, neglecting the diffusion potentials:

$$E = \frac{RT}{F} \log \frac{C_1}{C_2} = 0.059 \log \frac{C_1}{C_2}$$

In these calculations we consider the dissociation of silver nitrate in 0.0001 N solution as being complete, which, of course, is not quite correct. The results of these estimates are given in Table VI.

TABLE VI

AgNO₃ Conc. of solution	Conc. of Ag-ion	Percentage dissociation
0.0001	0.0001	100
0.001	0.00079	79
0.01	0.0039	39
0.1	0.018	18
0.2	0.028	14
1.0	0.066	6.6
1.5	0.123	8.2
2.0	0.231	11.6

From the electrometric measurements as is seen from the table we can also draw the conclusion that *the degree of dissociation of silver nitrate in pyridine passes through a minimum in accordance with the results of measurements of conductivity.* Since only corrected molecular conductivities (L) give minimum values, therefore, the expedience of the suggested corrections for the change of viscosity is proved.

There is a striking difference between the position of the minimum according to the data of conductivity and that as shown by the electromotive forces. In the first case we ob-

tain a minimum at a dilution of 15 liters and in the second at a dilution of 1 liter. Such difference from the point of view of the theory of current conducting complexes could be foreseen, since the formation of complex cations of silver must inevitably produce this difference. This question will be particularly treated in our next investigation.

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THE ADSORPTION OF CHROMIUM OXIDE BY HIDE POWDER

BY A. W. DAVISON

The question as to the constitution of leather is still a widely debated one. The adherents of the chemical compound theory on the one hand are pitted against the supporters of the physical adsorption theory on the other. Neither faction is ready to accept, in their entirety, the claims of the other. As a representative of those supporting the chemical compound viewpoint, Fahrion[1] points out that leather is a salt, in which the oxidized hide, being amphoteric in character, may play the role of either acid radical or basic radical; and the tanning agent, that of basic or acid radical. Whether the hide functions as acid or base will depend solely upon the character of the tanning agent.

The adherents of the physical adsorption theory believe that the changes wrought in hides by tanning are of a physical, rather than a chemical nature; and that they are analogous to those brought about in cotton by mercerization; rubber by vulcanization; or in cellulose by nitration; all of which are now regarded as adsorption phenomena.

Some authors go a step farther, and claim that although the process of tanning is one of adsorption, pure and simple, further slow changes may take place with time. Stiasny[2] holds that since in the majority of cases tan stuffs are taken up from their colloidal solutions, the adsorption becomes immediately irreversible. He does not deny that slow chemical reactions may later take place between the hide fiber and the tanning agent.

As a preliminary to some extended work on the theory of tanning which is to be carried on in this laboratory, it was deemed desirable to substantiate, if possible, the claims of the physical theorists that the first process in tanning is one

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[1] Zeit. angew. Chem., **22** (2) 2083, 2135, 2187 (1909).

[2] Zeit. Kolloid Chem., **2**, 257 (1908).

of straight adsorption. Further, and later changes, of whatever nature, are without the province of this paper.

The author has chosen the phase rule method of attack, because it so readily lends itself to the solution of problems of this character. Chromium has been selected as the tanning agent, since it, as a typical metallic tan, affords ease and certainty of analysis.

Although chromium salts are known to harden gelatine,[1] it was believed to be more advisable to use hide powder as the adsorbing agent, for the reason that one would thereby be working nearer to actual tanning conditions; and he could be more certain of dealing with a uniform, readily replaceable material. The hide powder used was the variety known as American Standard, obtained from Daigger and Company, Chicago. Although this product is somewhat coarse, it was found to be sufficiently porous to be thoroughly permeated by the tanning solutions. The powder was kept in a tightly closed metal can, and was weighed directly, without previous treatment, into the shaking flasks.

The tanning solution was made after a "single bath" formula by Flemming.[2] Transposed into the metric system, this formula calls for: Solution A Chrome alum, 120 g in 1000 cc water; Solution B Sodium carbonate, 30 g in 100 cc water. Solutions A and B are to be slowly mixed, and any resulting precipitate removed by filtration. Throughout the remainder of this article, the resulting solution is called "strong tan solution."

The final solution in which hides are to be tanned consists, for, say, ten kilograms of wet skin:

Strong tan solution	2.5 liters
Water	66.3 liters
Salt	70.0 grams

After the tanning process has been going on an hour, two and a half additional liters of strong tan solution should be added: this addition of strong tan solution should be con-

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[1] Neuner: Zeit. Kolloid Chem., **8**, 144 (1911).

[2] "Practical Tanning," p. 225.

tinued until the hides are fully tanned. In all, about eight liters of strong tan solution are said to be required for ten kilograms of skin.

In order that conditions in all of the tanning flasks might be perfectly uniform, it seemed desirable to complete the impregnation of the hide fibers at one operation. The usual method of "strengthening up" the solution after each hour leaves entirely too much uncertainty of equilibrium. Then, too, when one is dealing with powdered hide, which has previously been soaked in salt water, there is no tendency toward "case hardening," or uneven tanning, because the solution so easily permeates the entire fibrous mass. At least, in these experiments, microscopic examination of the tanned powder failed to reveal uneven tanning.

The soaking and tanning operations were carried out in five hundred cubic centimeter, rubber stoppered, Erlenmeyer flasks. These were clamped to a rotating device in such a manner that the flasks were turned about a horizontal shaft perpendicular to their axis of symmetry. The radius of rotation was twelve inches; the flasks revolved fifty times per minute. This insured perfect agitation, since the total volume of solution in each five hundred cubic centimeter flask was only two hundred and seventy-five cubic centimeters. The whole device was immersed in a thermostat at 28° C.

Two grams of hide powder were weighed directly into each flask, and two hundred and fifty cubic centimeters of salt solution, containing ten grams of sodium chloride per liter, added. The flasks were then rotated for one hour, in order to insure perfect and uniform soaking of the material. Then the strong tan solution was introduced. The actual amount of tan liquor added is of little import, since interest centers only around concentrations at equilibrium, and the solutions were all to be analyzed at a later stage. The volumes varied roughly from one to twenty-five cubic centimeters. Since it was highly necessary to hold the salt concentrations in the various flasks constant, the tan liquor added was in every instance diluted to twenty-five cubic centimeters. Thus

in the case of the flask to which ten cubic centimeters of strong tan solution were to be added, fifteen cubic centimeters of distilled water were mixed with the chrome liquor before the latter was added to the tan flask. The conditions in all flasks were, therefore, the same, except for varying amounts of tan liquor.

The tanning process proper was run for four hours. Preliminary experiments showed that equilibrium was fully established in that time: Two gram portions of hide powder were soaked one hour, then tanned for varying times, using in each instance twenty cubic centimeters of strong tan solution. At the end of each hour, a flask was removed, and the solid phase analyzed. The results are shown in Table 1.

TABLE 1

Hours in contact with tan liquor	Weight Cr_2O_3 in solid phase
1	0.1795
2	0.2038
3	0.2093
4	0.2120
5	0.2115
6	0 2117

It will be noticed that after four hours there was a loss in the weight of Cr_2O_3 found. This may be attributed to experimental error, or it may be caused by disintegration and solution of the finer particles of tanned powder after so long a time in the rotating device.

The separation and analysis of the different phases under consideration presented by far the most difficult and perplexing problem. In order to obtain concordant results, there must be no solution adhering to the tanned powder, and the latter required quantitative treatment. Once tanned, however, hide powder is not difficult to operate upon; it does not tend to stick to chemical glassware, neither does it present serious difficulties in filtration. However, the removal of adhering solution requires the utmost care. Washing with any solvent whatever is entirely impossible; hence some simple

A. W. Davison

method of mechanical separation was desired. The author believes that the problem was solved, within reasonable limits of error, by first filtering off the solid phase, then removing the adhering liquid with a centrifuge. Had it been possible to use the centrifuge alone, more accurate results might have been secured, because the uncertain amount of chromium adsorbed from the solution by the filter paper would have been eliminated. Unfortunately, when one attempted to run the solution containing the tanned powder directly into the centrifuge while it was rotating, small particles of leather clogged the orifice.

A number of methods for obtaining a rough separation, giving a solid-liquid mixture of sufficiently small volume to be introduced into the stationary centrifuge, were tried; but the only successful one consisted in filtering off the solid phase on small four centimeter Büchner funnels, using hardened filter paper, and removing the last particles of tanned powder from the Erlenmeyers by washing with some of the solution which had already been through the filter. This rough separation could easily be effected in twenty minutes. The liquid at this point was saved for analysis. The solid phase still contained considerable solution, but the maximum amount of this could now be removed with the centrifuge. The latter was the usual Dulin Rotarex laboratory type. Each sample, after being carefully separated from the small disc of filter paper, was centifuged thirty minutes, at the maximum speed; and at the end of that time the assumption had to be made that they were uniformly dry. It has been pointed out by Leighton[1] that where one is dealing with dilute solutions, the nature of an adsorption curve is changed but little, when there is a marked difference in the amount of water adsorbed by the solid phase at different concentrations of the liquid phase. Since extreme care was exercised in the centrifugal process in order to secure uniformity of drying, it was not deemed advisable or necessary to determine the actual amount of water taken up in every instance.

[1] Jour. Phys. Chem., 20, 47 (1916).

The concentration of chromium in the solutions at equilibrium was determined volumetrically. The chromium in aliquot portions of each solution was oxidized by boiling with sodium peroxide, and converted into sodium dichromate, with acid. A measured excess of tenth normal ferrous ammonium sulphate was run in, and the unoxidized iron determined with tenth normal dichromate, using diphenylcarbazide for indicator.[1]

These concentrations represent true values at equilibrium, except for the small amounts of chromium solution adsorbed by the filter papers in the Büchner funnels. Analyses of these papers showed the amount of water, and chromium, taken up by so small a disc to be entirely negligible when compared to the large volume of solution (two hundred and seventy-five cubic centimeters) dealt with.

In Table 2, concentrations of the solutions are expressed in terms of the number of cubic centimeters of tenth normal ferrous ammonium sulphate equivalent to the dichromate from one hundred cubic centimeter portions of the liquid phase.

At first the chromium in the solid phase was determined as follows: The tanned hide powder was dried at 80°, pulverized, and fused with sodium peroxide, in nickel crucibles. The resulting mass was next dissolved in boiling water, acidified, and filtered. ' The chromium, now present as sodium dichromate, was determined by titration, as in the case of the liquid phase samples. But the quantitative fusion of so large a mass of tanned hide powder was found to be entirely too uncertain and troublesome, so a more simple method of analysis was devised. The dried product from the centrifuge was treated with a few cubic centimeters of nitric acid, placed in porcelain crucibles, and ignited at dull red heat in an electric furnace. This treatment burned out the gelatine of the hide, leaving behind the chromium oxide, sodium chloride, potassium sulphate, and the ash of the hide powder. The sodium chloride and potassium sulphate were washed out, and the residue weighed. This, minus the weight of the insoluble ash from two grams of

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[1] Jour. Am. Chem. Soc., **35**, 156 (1913).

hide powder, was called Cr_2O_3.   In Table 2, the concentration of chromium in the solid phase is given in grams of Cr_2O_3 taken up by two grams of hide powder.

Concentration values for both the liquid and the solid phase are given in Table 2.

TABLE 2

Concentration in liquid phase cc $n/10$ FeSO₄ equivalent to dichromate produced by chromium in 100 cc solution	Concentration in solid phase gm Cr_2O_3 adsorbed by 2 gm hide powder
0.08	0.0743
0.17	0.0873
0.43	0.1093
0.78	0.1238
1.49	0.1421
2.09	0.1591
3.12	0.1740
4.78	0.1940
6.29	0.2041
8.05	0.2120
11.37	0.2244
14.90	0.2352

When plotted, the results appear in Fig. 1.
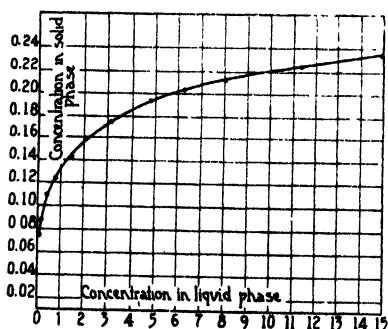
Fig. 1
Adsorption of chromic oxide by hide powder

An inspection of the curve will reveal the fact that no breaks, horizontal, or vertical portions, exist.   The phase

rule, therefore, tells us that we are dealing with an adsorption isotherm; and that no compounds between the hide powder and the tanning agent have been formed. In the case of chrome tanning, therefore, the contention of the physical theorists, that the first step is one of pure adsorption, has been verified.

The author desires to express his appreciation to Professor W. D. Bancroft for certain suggestions; and to Mr. E. K. Files, of this laboratory, for carrying out the analyses of the solid phases.

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ELECTRICAL ENDOSMOSE. I

BY T. R. BRIGGS

Electrokinetic effects in a system composed of liquid and finely divided solid were observed first by Reuss, working at Moscow in 1808. He inserted into a lump of moist clay two vertical glass tubes, filled them with water and dipped an electrode into each. On establishing a potential gradient between the electrodes, Reuss noticed to his surprise that the liquid rose in one tube and sank in the other, and that furthermore a decided turbidity developed in that tube in which the water level sank. There had occurred, in short, a transfer of liquid to the cathode through the more or less porous clay diaphragm and, besides this, a simultaneous migration of some of the detached clay particles, the effects taking place in opposite directions.

Reuss applied to these phenomena the somewhat terrifying expression "motus stoechiagogus," but fortunately this term was soon displaced by a more euphonious one. The change appears to have followed Porrett's experiments,[1] which showed an apparent analogy between osmosis and the Reuss effect; it became customary accordingly to refer to the electrical transport of liquid through a porous diaphragm as *electrical endosmose*. It is now customary to speak of the electrical migration of suspended particles as *cataphoresis*. One will find, however, much apparent confusion regarding the use of these terms, a situation which may possibly be due to du Bois-Reymond, who included at a later date *both* the Reuss effects under the caption "Kataphorische Wirkung des Stromes." Physicists[2] are especially likely to employ both terms interchangeably. I shall follow throughout this discussion the accepted usage and shall employ as a guide the classification proposed by Freundlich.[3]

[1] Thomson's Annals of Philosophy, 8, 74 (1816).
[2] Cf. Cruse: Phys. Zeit., 6, 201 (1905).
[3] Kapillarchemie, 223 (1909).

Electrokinetic phenomena in two phase systems of liquid and solid may be analyzed into four distinct processes, of which electrical endosmose and cataphoresis are the ones commonly met with. So far as the electric current is concerned we may distinguish two cases, as follows:

(1) *A difference of potential sending a current through the system may produce a relative displacement of the phases.*

(a) If the solid is fixed in the form of a porous diaphragm the liquid may move through the diaphragm. Electrical endosmose.

(b) If the solid is in the form of a suspension and is free to move, the solid may migrate through the liquid. Cataphoresis.

(2) *A relative displacement of the phases may produce a difference of potential and consequently an electric current through the system.*

(a) If the solid is fixed in the form of a porous diaphragm through which liquid is forced, a difference of potential and an electric current may be established between the extremes of the diaphragm. Quincke's diaphragm currents.

(b) If the finely divided solid is dropped through the liquid, a difference of potential and a current may be set up between the upper and lower liquid strata. Billitzer's experiments. This case resembles closely the drop electrode.

Wiedemann[1] was the first to carry out an extended study of electrical endosmose, and as a result of his researches he promulgated several fundamental generalizations, which are usually referred to as Wiedemann's laws:

(1) The mass of liquid transported in unit time through a porous diaphragm, is directly proportional to the strength of the electric current; and, for a given diaphragm material and given current strength, it is independent of the length and sectional area of the diaphragm.

(2) The difference in hydrostatic pressure maintained by electrical endosmose between the two sides of a porous

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[1] Pogg. Ann., **87,** 321 (1852); **99,** 177 (1856).

diaphragm, varies directly as the current strength, and for a given diaphragm material and a given current, is proportional directly to the length and inversely to the sectional area of the diaphragm; it is also proportional to the specific resistance of the liquid in the case of an aqueous solution.

By applying Ohm's law and the known relation between resistance and the dimensions of a conductor, Wiedemann was able to modify the second law as follows:

(3) For a given diaphragm material, the difference in hydrostatic pressure maintained between the two sides of a porous diaphragm is proportional to the applied potential and is independent of the dimensions of the diaphragm.

The phenomenon of "diaphragm currents" is the converse of electrical endosmose so far as we are concerned with the motion of the liquid through the diaphragm and with the electric current. The discovery of these currents was made by Quincke,[1] who measured the difference of potential and the current produced when he forced different liquids through an apparatus containing a porous diaphragm. His results are summarized briefly in the following generalization, which one may regard as the converse of Wiedemann's third law:

"When water is forced at a certain rate through a porous diaphragm, the difference of potential produced is independent of the dimensions of the diaphragm but is proportional directly to the applied hydrostatic pressure."

It is not my purpose to discuss in detail the theoretical and mathematical treatment of electrokinetics in systems such as we are considering. One should refer of course to the fundamental papers of Helmholtz,[2] who developed quantitatively and mathematically the hypothesis of the electrical double layer, which Quincke had already suggested in a qualitative way.

Under most circumstances, solids and liquids become electrically charged, apparently merely by contact. The distribution of the charges is such that an electrical double

[1] Pogg. Ann., **107**, 1 (1859); **110**, 38 (1860).
[2] Wied. Ann., **7**, 337 (1879) *et seq.*

layer is established on the solid and on the layer of liquid with which it is in contact. Under the influence of a potential gradient applied externally, there occurs a displacement of the electrically charged layer of liquid and, if the liquid is not a perfect insulator, the displacement results in a continuous flow[1] of liquid along the surface of the solid and a steady reëstablishment of the electrical double layer.

Freundlich,[2] following a treatment used by Perrin, develops the following expression for the amount of liquid (V_e) transported electrically in unit time through a single capillary tube:

$$V_e = \frac{\pi r^2 \epsilon E D}{4 \pi \eta l} \qquad (1)$$

In this expression E is the total fall in potential through the capillary; D and η are, respectively, the dielectric constant and the viscosity coefficient of the liquid and ϵ is the potential of the Quincke-Helmholtz double layer at the solid-liquid interface. If, instead of a single capillary of length l and diameter $2r$, one employs a porous diaphragm and imagines this to be equivalent to a bundle of capillaries $\Sigma \pi r^2$ may be considered as being proportional to q, the cross-sectional area of the diaphragm. Equation 1 then becomes:

$$V_e = \frac{q \epsilon E D}{4 \pi \eta l} \qquad (2)$$

Now, since $E = RI$ and $R = l/\gamma q$, where γ is the specific conductivity of the liquid, Expression 2 may be modified to the following:

$$V_e = \frac{\epsilon I D}{4 \pi \eta} = \text{constant } x \, I \qquad (3)$$

whence it is evident that the amount of electro-osmose—for a given liquid and a diaphragm—is independent of the latter's dimensions and is proportional to the current strength. Equation 3 becomes thus a mathematical expression of Wiedemann's first law.

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[1] Compare also Lamb: Phil. Mag., (5) **25**, 52 (1888).

[2] Kapillarchemie, 225 (1909).

Returning to the simple case of a single capillary, one may measure the difference in hydrostatic pressure produced by electro-osmose, rather than the volume of liquid transported. When equilibrium results, there must occur a balance between the transport of liquid in one direction by endosmose, and the flow of liquid in the opposite direction under the influence of the resultant hydrostatic pressure. Poiseuille's law holds for the second process, and, according to this law

$$V_p = \frac{\pi r^4 P}{8\eta l},$$

in case the length of the capillary is large compared with its internal diameter ($2r$). P is the difference in hydrostatic pressure between the two extremes of the capillary. Since for equilibrium V_p must be equal to V_e corresponding to Expression 1, the following equation describes the difference in hydrostatic pressure produced by electro-osmose in a narrow capillary:

$$P_e = \frac{2\epsilon ED}{\pi r^2} \qquad (4)$$

One should observe that in this expression q may no longer be substituted for πr^2 and the equation in that form applied to the case of a diaphragm. For Poiseuille's law is limited in its application to narrow capillaries (see above). As a matter of fact, so long as the average size of the particles of a diaphragm remains constant the mean cross-sectional area of the pores may be safely regarded as unchanged and πr^2 as a constant, say, k. Accordingly Equation 4 reduces to the following:

$$P_e = \frac{2\epsilon ED}{k} = K_o E \qquad (5)$$

That is, for a given liquid the hydrostatic pressure produced by electrical endosmose through a given diaphragm of definite structure (porosity, etc.) is proportional to the total fall in potential through the diaphragm and is independent of the latter's dimensions. This is a modified statement of Wiedemann's third law and agrees satisfactorily

with the experiments of Quincke,[1] who measured the rise of a liquid in a single capillary of glass.

An overwhelming majority of the earlier experiments showed the water or aqueous solution moving to the cathode through the diaphragm. Having accepted the hypothesis of an electrical double layer, everybody concluded that the immovable layer on the solid was negative while the one free to move was positive. Accordingly the rule was suggested that *all solids become charged negatively when placed in contact with water or an aqueous solution.* Perrin[2] was the first to show conclusively that this rule fails to hold in a large number of cases.

In his study of diaphragm currents, Quincke used a variety of powdered solids and several different liquids. Against water every solid appeared to be electronegative, the intensity of electrification varying within wide limits in the order: Sulphur > quartz > shellac > silk > Daniell cell standard > burnt clay > asbestos > porcelain > ivory shavings > animal membranes, etc. Against turpentine these same solids were electropositive with the single exception of sulphur which remained weakly negative.

Coehn[3] has taken up the question as to why there exist differences such as these which Quincke described and he has proposed the following empirical rule:

When two non-miscible substances, one of which is a pure liquid, are in contact, the substance with the higher dielectric constant is positive against the substance with the lower.

Quincke's data appear intelligible in the light of Coehn's rule. Water and turpentine have dielectric constants of 81 and 5, respectively. Furthermore, the constant in the case of water is one of the largest known and we should expect nearly every substance to be electronegative against water. In the case of turpentine, however, many substances ought to

[1] Pogg. Ann., **113,** 513 (1861).

[2] Jour. Chim. phys., **2,** 601 (1904).

[3] Wied. Ann., **64,** 227 (1898); Zeit. Elektrochemie, **16,** 586 (1910).

be electropositive, and this is what one finds to be actually the case.

In discussing Coehn's results, one must record some curious things. Glass should have been negative against glacial acetic acid but became positive on long standing in contact with this liquid. Likewise with propionic acid. In the case of xylol, toluol and other liquids where D is small, the electrical endosmose occurred so slowly as to be negligible. Coehn accordingly added a trace of hydrochloric acid to improve the conductivity, endosmose occurred and the glass became charged positively against the liquid. Acid added to the other liquids made the glass *less* negative. It seems a question, therefore, whether the positive charge on glass in contact with xylol, toluol, etc., may not be due as much to the hydrochloric acid present as to the very small dielectric constants of these liquids. This point needs to be settled experimentally.

The Effect of Dissolved Substances upon Electrical Endosmose

A few years after Reuss had performed his original experiment, Porrett[1] rediscovered the phenomenon of electrical endosmose. His apparatus consisted of a glass cell divided into two compartments by an animal membrane, containing platinum electrodes; having filled the whole system with water he observed a flow of liquid into the cathode chamber when the circuit was closed through a voltaic pile. He found also that when dilute sulphuric acid took the place of water, the flow of liquid fell nearly to zero.

Daniell,[2] while engaged in his classic electrolyses of the alkali salts, took up casually a study of electrical endosmose. A solution of sulphate of soda (sp. gr. 1.052) flowed to the cathode through a porous cup, on the application of about 30 volts. A difference in level of 1.5 in. was produced between the two sides of the diaphragm. Distilled water and

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[1] Thomson's Annals of Philosophy, **8**, 74 (1816).

[2] Phil. Trans., **129**, 97 (1839).

sodium phosphate (sp. gr. 1.057) rose half an inch and two inches, respectively, the flow being toward the cathode in each case. A very dilute solution of sulphuric acid rose only a quarter of an inch; a stronger solution gave no flow at all. He concludes as follows:

"Notwithstanding the good conducting power, however, of the saline solutions, we have seen that this passage of liquid from the zincode [anode] to the platinode [cathode] occurs with them even to a greater extent than with pure water; and the different species of salts seem to be acted upon in different degrees."

The majority of Wiedemann's experiments were carried out with a tubulated porous cup containing the cathode, and the endosmose was determined directly from the amount of liquid transported in unit time. Solutions of sodium, potassium, zinc, and copper sulphates were studied with results which led Wiedemann to say:

"In general the greater the resistance of a liquid the greater is the amount transported under the same conditions of current strength."

In every cell, the liquid moved to the cathode. A second and very correctly conceived apparatus enabled Wiedemann to extend the study to certain other porous septa, such as gypsum, earthenware, and animal membrane. Flow to the cathode was the rule, except when sulphuric acid was present; for solutions of this acid, even when dilute, showed no electrical endosmose.

Quincke added various solutes to the water which he pumped through his porous diaphragms. When dilute sulphuric acid was forced through porous earthenware, the diaphragm current fell to zero, exactly as one should expect from what has gone before. On the other hand, the current was increased by adding alcohol to the water. Caustic soda or copper sulphate (in unknown amounts) weakened the deflection of the galvanometer needle. With powdered sulphur both nitric acid and sodium chloride reduced the current normally produced by distilled water. Mineral waters gave

a smaller diaphragm current than distilled water; on the other hand tannin extracted from oak sawdust, as well as soap, increased the current generated with a diaphragm of powdered glass.

Quincke sums up his work as follows:

"By the addition of acids or salts to distilled water the direction of the electric current was not changed, but the intensity of the current was reduced until it became no longer noticeable."

With a porcelain diaphragm and solutions of sodium chloride Quincke obtained the following data, which show how marked are the changes which occur:

Concentration (g per 100 cc)	E. M. F. per atmosphere (compared to Daniell cell = 1)
0.00	0.69
0.025	0.11
0.05	0 076
0.5	0.041

Aqueous alcohol, when forced through an earthenware diaphragm, increased the E. M. F., as we have seen already, but in this case we have the further observation that the exit liquid was appreciably richer in alcohol than that which entered. Quincke appears to have observed a case of negative adsorption, so-called.

In his third paper Quincke took up electrical endosmose and cataphoresis. His experiments on electrical endosmose were carried out in a single capillary tube, slightly inclined from the horizontal. A Leyden battery furnished the applied potential and produced a rise of liquid in the capillary proportional to the potential in any given case. Measurements of this kind were found to be influenced very strongly by dissolved substances and impurities. It was found that alkali and other material dissolved from the glass could not be ignored. Dissolved substances always produced a marked decrease in the electrical endosmose.

In every case studied up to Quincke's time the endosmotic flow had been invariably from anode to cathode, or the equivalent of this in the case of "diaphragm currents." Endosmose to the anode was observed by Quincke with turpentine, as we have seen, and sometimes with carbon bisulphide. Furthermore he found that a particular mixture of alcohol and water flowed to the anode; on adding more water the *direction* remained the same while the *rate of flow diminished*. Had Quincke added enough water, he would presumably have obtained a change in direction after passing through a point of zero flow (isoelectric point) since pure water always went to the cathode. He ascribed this unusual result to some impurity in the alcohol, for other samples failed to give the same effect.

Munck is reported by Wiedemann[1] to have obtained reversal of flow to the anode with dilute solutions of both neutral and acid K_2CrO_4, but these results were contradicted by Gore[2] who failed to obtain reversal in either of the above cases. Gore observed that saturated solutions of barium bromide in alcohol went to the anode but no similar case was met with among a large number of aqueous solutions. Indeed, the usual flow to the cathode is reported in all but one instance (saturated solution of KCN), and even in the case of comparatively strong sulphuric acid! Gore's data are very unsatisfactory, however, since no clue as to the relative intensity of electro-osmose is given in the original paper, nor are there any experimental details; the diaphragms were composed of porous "biscuit ware" and the current was obtained from a battery of Grove cells.

Certain interesting experiments have been described by Gernez,[3] who observed a "creeping" action on the part of a film of water wetting the inner surface of a glass capillary, under the influence of the current from a Holtz machine. In every case the movement of the liquid film appeared to be

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[1] Elektricität, **2**, 153 (1883).
[2] Proc. Royal Soc., **31**, 253 (1880).
[3] Comptes rendus, **89**, 303, 348 (1879).

toward the negative side and to be contingent upon the surface being wetted; if the latter condition was not fulfilled no motion occurred. It was proven, furthermore, that the transfer of liquid could in no wise be due to a process of distillation between the two oppositely electrified arms of the U-tube employed. The transfer of liquid in this case seems to be identical with that observed by Lemström[1] and employed by Freundlich in some experiments which will be discussed presently.

Gernez was quick to perceive the retarding tendency of dissolved substances, for he says: "On the other hand the addition to pure water or to alcohol of substances which change the conductivity of these liquids has for an effect a very sudden decrease in amount of liquid transported; when one adds to distilled water a few drops of an acid, such as sulphuric, nitric or hydrochloric, in quantity too small to produce any measurable change in density or temperature of ebullition, the speed of transport is reduced to a fraction of its original value, often to less than one-fiftieth. The alkalies, such as potash or ammonia, employed in very small amounts produce the same effect. The same thing occurs with solutions of neutral salts. . . .

"I may add in the meantime that if one submits a homogeneous mixture of two liquids to the influence of the discharge the action of the electricity causes a partial separation of the two liquids, which distill in proportions which are in agreement neither with the volatility nor with the conducting power of each substance. Thus in working with a mixture of alcohol and water, one obtains by electric separation a liquid less rich in alcohol than the residue."

Although electrical endosmose and its related subjects were investigated experimentally by others following after Quincke—notably by Freund[2] and Saxen[3]—little of especial interest and importance with regard to osmose in conducting

[1] Drude's Ann., **5,** 729 (1901).
[2] Wied. Ann., **7,** 53 (1879).
[3] Ibid., **47,** 46 (1892).

solutions was announced until Perrin's[1] paper made its appearance. Perrin devised an ingenious and very simple electro-osmometer, which, though not entirely free from defects, possessed nevertheless the great advantage of permitting the study of many different solid materials. The material of which these diaphragms were constructed was employed in the form of a fine powder and special precautions were observed in its preliminary treatment. The care shown in regard to this point marks Perrin's work as far in advance of all that had preceded it, for uncertainty as to the condition of the diaphragm detracts from the value of much of the earlier work.

The pulverized solid was used in the form of a cylindrical diaphragm in a vertical glass tube which constituted one arm of a large U-tube. Platinum electrodes were sealed in close to the upper and lower extremities of this diaphragm. The rate and direction of endosmose was determined from the movement of a liquid meniscus in a calibrated capillary, inclined slightly from the horizontal, and joining the body of the apparatus just above the diaphragm. For each experiment a freshly prepared and washed diaphragm was used, and care was taken to have it reach a state of equilibrium in the solution to be studied. Although Perrin's apparatus was not adapted to absolute measurements, very useful comparative data were obtained with an ease hitherto unknown.

A preliminary study was made on the effect of temperature changes. As the temperature in the diaphragm rose, the volume of liquid transported increased rapidly *and it was assumed that the temperature had the same effect upon the flow as it had on the fluidity (reciprocal of viscosity) of the liquid.* No data were given, however, and we shall find later that Perrin's conclusions regarding this point were only approximately true.

Coehn and Raydt[2] have studied the temperature coeffi-

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[1] Jour. Chim. phys., **2**, 601 (1904); Comptes rendus, **136**, 1388, 1441; **137**, 513, 564 (1903).

[2] Drude's Ann., **30**, 797 (1909).

cient, employing the rise in a capillary tube, which by Equation 4 is independent of the viscosity. They found a relatively small *negative* temperature coefficient equal approximately to the negative coefficient of the dielectric constant. Cameron and Oettinger[1] measured the diaphragm potential obtained by forcing an $N/3000$ potassium chloride solution through a capillary under constant pressure. Between $21°$ and $31°$ C the potential fell off by about 3 percent—a result confirming Coehn's data very satisfactorily.

On the other hand, Cruse[2] has come to entirely different conclusions. Using a porous earthenware diaphragm, he found that "the electro-cataphoresis [electro-osmose] of distilled water, with increasing temperature, rises to a maximum lying between $35°$ and $40°$ C; thereupon it falls off and above these temperatures decreases rapidly at first and then slowly."

Perrin turned his attention next to the effect of dissolved substances. His first conclusion was that electrolytes alone influenced the electrical endosmose and that the ions were of course the active agents. Mere traces were sufficient to produce powerful effects in many cases, while under constant conditions of temperature and concentration, the activity of the different ions varied within wide limits.

It soon became evident that the degree of acidity or alkalinity of the solution was one of the important factors. With a diaphragm of insoluble chromic chloride (violet), acids flowed to the anode and alkalies to the cathode—a case of marked reversal. Similar reversals were obtained with diaphragms of alumina, carborundum, sulphur, gelatine, graphite, naphthalene, etc. The data for naphthalene follow. The numbers under "Flow" refer to a transport in cubic millimeters per minute caused by a potential gradient of 10 volts per centimeter through the diaphragm:

[1] Phil. Mag., (6) **18**, 586 (1909).
[2] Phys. Zeit., **6**, 201 (1905).

NAPHTHALENE DIAPHRAGM

Solution	H· conc.	OH′ conc.	Diaphragm charged	Flow
$n/50$ HCl	$2 . 10^{-2}$	$5 . 10^{-13}$	$+$	38 to anode
$n/100$ HCl	10^{-2}	10^{-13}	$+$	39 to anode
$n/1000$ HCl	10^{-3}	10^{-11}	$+$	28 to anode
$n/5000$ HCl	$2 . 10^{-4}$	$5 . 10^{-11}$	$+$	3 to anode
$n/5000$ KOH	$5 . 10^{-11}$	$2 . 10^{-4}$	$-$	29 to cathode
$n/1000$ KOH	10^{-11}	10^{-3}	$-$	60 to cathode
$n/50$ KOH	$5 . 10^{-13}$	$2 . 10^{-2}$	$-$	60 to cathode

These results at first led Perrin to underestimate the apparent specific effect of the diaphragm material, for his initial approximation was as follows:

"In the absence of polyvalent radicals, every non-metallic substance is positive in an acid liquid and negative in an alkaline."

Perrin soon found exceptions to this rule. Both acid and alkali flowed to the cathode through cotton wool (cellulose). However, as the strength of the acid increased, the flow decreased until it became zero at a concentration of one-thirtieth normal in the case of hydrochloric acid. This corresponds to an isoelectric point for the diaphragm. Were the rule correct as stated above, the isoelectric point should coincide with the point of exact neutrality, or, in other words, pure water should show no electrical endosmose through any diaphragm.[1]

Iodoform and glass diaphragms were even more persistently electronegative, while barium carbonate and, to a less extent, chromic chloride, possessed distinctly electropositive characteristics. On analyzing Perrin's data it will be

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[1] Cf. Coehn: Zeit. Elektrochemie, **16**, 586 (1910); Cameron and Oettinger: Phil. Mag., (6) **18**, 586 (1909).

found that in no case does the isoelectric point correspond to exact neutrality, although this condition is approached closely in some instances (alumina, naphthalene, etc.). Accordingly Perrin was obliged to modify his first statement to the following:

"The electric potential of any surface whatever in aqueous solution is invariably increased by the addition of a monovalent acid to this solution, and it is always lowered by the addition of a monovalent base."

I wish to point out in passing that Perrin's modification of his original hypothesis has been overlooked by many of his critics, notably by Cameron and Oettinger and by Coehn. Indeed, Coehn went so far as to prove that water of exceptional purity gave electrical endosmose through a short capillary tube bored in diamond.

To be sure, Perrin thought the substance and nature of the diaphragm were of little importance and he believed the differences were best explained by postulating different solubilities in water. If the ion content (especially the acidity or alkalinity) of the liquid is changed by the solid dissolving, one would expect measurable differences in the endosmose, since the contact potential is so extremely sensitive to traces of dissolved substances. My own belief is in a way like Perrin's, except that it goes one step farther and postulates preferential or selective adsorption of the ions, which is a property distinctly characteristic of every solid.

Perrin considered next the effect of other ions. Instead of employing relatively strong, *neutral* solutions of various salts, he used dilute solutions rendered slightly acid or alkaline. His method was equivalent to studying the influence of other ions upon the known effects produced by hydrogen and hydroxyl ions. The results follow:

When the diaphragm is *positive*, anions are more active than cations; when the diaphragm is *negative*, the reverse holds true. In general, every anion *lowers* the positive charge on a diaphragm, producing concomitantly an effect upon the electrical endosmose. This effect is shown by a falling off

in the flow per minute and it seems to be greater in many instances the higher the valence of the active ion. Cations have the same effect on a negative diaphragm.

Freundlich[1] has calculated from Perrin's data the concentration of salt in millimols per liter necessary to reduce by one-half the endosmose through a positive diaphragm, the salt being added to a dilute hydrochloric acid solution of constant composition. In this case the anions were active.

I. CHROMIC CHLORIDE DIAPHRAGM (POSITIVE)

Solution	Active ion	Half-value
Dilute acid + KBr	Br'	60
Same acid + MgSO$_4$	SO_4''	1
Same acid + K$_3$Fe(CN)$_6$	$Fe(CN)_6'''$	0.1

Similar data were obtained with a carborundum diaphragm in dilute alkali, except that in this case the cations were active.

II. CARBORUNDUM DIAPHRAGM (NEGATIVE)

Solution	Active ion	Half-value
Dilute alkali + NaBr	$Na\cdot$	50
Same + Ba(NO$_3$)$_2$	$Ba\cdot\cdot$	2
Same + La(NO$_3$)$_3$	$La\cdot\cdot\cdot$	0.1

I wish to call attention to the apparently abnormal activity of the particular polyvalent ions studied by Perrin and the resemblance shown to the rule of Schulze and Hardy.[2] Perrin found the influence of polyvalent ions of unlike charge to be great enough to reverse the direction of osmose in some instances. A reversal of this kind means, of course, that the sign of the interface potential has been changed. Perrin gives an interesting example in the case of a chromic chloride diaphragm and acidified potassium ferricyanide.

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[1] Kapillarchemie, 238 (1909).
[2] Cf. Bancroft: Jour. Phys. Chem., **18**, 24 (1914).

Solution	Diaphragm charged	Flow
Water slightly acid	$+$	59
Same $+$ 0.001 n/K$_3$Fe(CN)$_6$	$+$	2
Same $+$ 0.02 n/K$_3$Fe(CN)$_6$	—	20 (reversal)

Perrin's rules may be summarized as follows: Every diaphragm tends to become charged positively against an acid solution and negatively against an alkaline solution. Every ion of unlike sign tends to neutralize the charge on the diaphragm and this tendency increases rapidly with the valence of the ion.

Electrical endosmose with methyl alcohol has been studied by Baudouin.[1] The experiments were carried out in Perrin's electro-osmometer and it was found that alkali alcoholates in alcohol are equivalent to alkali hydroxides in water, the diaphragms tending to become negative. Acids act in methyl alcohol as they do in water, and polyvalent ions conform to Perrin's second rule.

Some interesting experiments are due to Larguier des Bancels[2] who used textile materials for his diaphragms in Perrin's apparatus. All three of the substances employed were electro-negative against distilled water in the order: wool > silk > cotton, and the negative charge was augmented by traces of alkali. In acid solution, however, silk was the only one of the three to show reversal, cotton and wool still being electro-negative against n/100 hydrochloric acid. These results with cotton confirm Perrin's observations with cellulose.

Furthermore, the action of polyvalent ions was entirely in accordance with Perrin's rule. By mordanting cotton with tannin and wool with bichromate the electro-osmose was not appreciably affected; but in some instances the dyed fibers behaved quite differently, notably when treated with magdala red or methylene blue (basic dyes). Wool dyed with these

[1] Comptes rendus, 138, 898 (1904).
[2] Ibid., 149, 316 (1909).

substances was much less electro-negative against water than the undyed material.

Perrin's laws of contact electrification have been confirmed more recently in a most interesting fashion by the so-called Bose-Guillaume phenomenon.[1] If two wires, one of which is covered with a very thin coat of some porous material, such as gelatine, be placed into a solution and the coated wire be given a sudden twist, a momentary E. M. F. is produced which may be detected by connecting the wires through a ballistic galvanometer. According to the most plausible explanation, liquid is squeezed out of the pores of the material coating the wire and, since the liquid is charged oppositely to the solid by contact, a momentary separation of electricities occurs and a difference of potential is produced. If the porous coating is negative against the liquid, the wire over which it is spread becomes negative against the uncoated wire and a current flows through the galvanometer. The Bose-Guillaume phenomenon is thus a special case of Quincke's diaphragm currents and since the latter are to be regarded as the converse of electrical endosmose, Perrin's rules should apply. Guillaume found that such was the case, using platinum wires coated with gelatine or fire-hardened clay. Some of his data follow:

BOSE-GUILLAUME EFFECT (PT COVERED WITH GELATINE)

Solution	Coated wire charged	E. M. F.	Active ion
NaOH 0.001 N	—	33.7	OH'
HCl 0.001 N	+	36.0	H·
Alkali + Na_2SO_4 0.001 N	—	31.8	Na·
Same + $K_4Fe(CN)_6$ 0.001 N	—	39.6	K·
Same + $Ba(NO_3)_2$ 0.001 N	—	19.1	Ba··
Same + La(NO) 0.001 N	—	2.5	La···
Same + more $La(NO_3)_3$	+	(reversal)	La···
Acid + Na_2SO_4 0.001 N	+	15.8	SO_4''
Same + $K_4Fe(CN)_6$ 0.001 N	— (reversal)	35.5	$Fe(CN)_6''''$
Same + $Ba(NO_3)_2$	+	36.0	NO_3'

[1] Guillaume: Comptes rendus, **147,** 53 (1908); Perrin: Ibid., **147,** 55 (1908).

Against an alkaline solution in the absence of disturbing polyvalent radicals, the twisted wire was charged negatively. In such solutions polyvalent cations, such as Ba' ' or La' ' ', neutralized the negative electrification to a great extent; when present in sufficient amount, the lanthanum salt produced reversal. It is interesting to note that the polyvalent anion $Fe(CN)_6$' '' increased the negative charge produced by alkali and more than neutralized the effect of the potassium ions. Guillaume's data would have been more useful had he used salts with a common anion or cation, as the case demanded.

The twisted wire was charged positively against hydrochloric acid solution and, when polyvalent anions were present, the E. M. F. fell off. The tetravalent $Fe(CN)_6$'''' ion was extremely active, producing a very marked reversal—indeed an acid solution of potassium ferrocyanide appeared to be equivalent to an alkali hydroxide so far as the electrification was concerned.

Ascoli[1] has studied electrical endosmose with liquid ammonia. Alumina was positive against the pure liquid but became negative when sodium was added.

Morse and Horn[2] have reported strong electrical endosmose through a porous cup in which they were depositing electrochemically a copper ferrocyanide membrane. They made use of this observation to remove air from the porous cup, before impregnating the latter with the membrane. They observed that "the liquid in the cup rises with a rapidity which increases with the dilution of the solution and the intensity of the current." These experiments led probably to a subsequent investigation of electrical endosmose by Frazer and Holmes,[3] whose work I shall discuss in some detail.

Frazer and Holmes designed elaborate apparatus, the diaphragms of which were porous earthenware, so that their

[1] Comptes rendus, **137**, 1253 (1903).
[2] Am. Chem. Jour., **26**, 801 (1901).
[3] Ibid., **40**, 319 (1908); H. N. Holmes: Dissertation (Johns Hopkins, 1907).

data apply to this particular material only. They studied very dilute solutions of alkali and alkaline earth nitrates and came ultimately to the following conclusion:

"The rule which is tentatively advanced is that the amount of osmose of various salts with a common anion varies approximately inversely as the velocity of the cation divided by its valence."

The data given to substantiate this statement were comparative and represented the amount of endosmose of various thousandth normal solutions as compared with potassium nitrate of equivalent strength, the flow of which was taken equal to 100. The numbers seem to confirm Frazer's rule very satisfactorily for the particular diaphragm material which they used, but before this rule can be accepted as a general one, it will have to be submitted to a much more rigorous test. The data were tabulated in the following form:

I $N/1000$	II Osmose	III Calculated osmose	IV Relative specific resistance
KNO_3	100.0	100.0	100.0
$NaNO_3$	149.1	148.4	120.7
NH_4NO_3	102.9	101.6	98.7
$LiNO_3$	182.6	187.3	139.6
$CsNO_3$	96.6	95.2	—
$RbNO_3$	96.9	95.2	—
$Ca(NO_3)_2$	64.8	66.6	113.8
$Sr(NO_3)_2$	61.3	65.1	114.3
$Ba(NO_3)_2$	58.4	61.0	108.9

In all cases where neutral salt solutions were employed, Holmes observed the usual flow to the cathode; but, on turning his attention to solutions of the common acids, he found reversals of the flow, just, indeed, as he should have expected. Such a reversal, and flow to the anode, was presented by solutions of acetic acid, which moved faster than hydrochloric. This is a bit surprising, for Perrin considered the rate of flow of acids with a monovalent anion to be an

approximate measure, at least, of their dissociation. Holmes' result is possibly quite correct, for one can easily reconcile oneself to such variations with the aid of the preferential adsorption hypothesis.

Holmes in his dissertation described a very interesting occurrence which apparently puzzled him a good deal, for he left it unexplained. However one does not have to seek farther than Perrin's experiments (which seem, by the way, to have been entirely overlooked by Holmes) to find a simple explanation which will account for all the facts. These I shall give in Holmes' own words.

"In one instance a $N/1000$ solution of barium nitrate, *when electrolyzed for some time* with the current at a potential of 100 volts, showed a slight but distinct 'negative osmose' [reversal of flow to the anode]. After the cell containing the barium nitrate had been refilled with some of the same solution and allowed to stand several hours, the usual positive osmose [to the cathode] was observed on closing the circuit."

The italics and brackets are mine. The anode was composed of sheet platinum and encircled the porous cup fairly closely. On closing the circuit the "positive" osmose carried the dilute barium nitrate solution through the cell walls into the cathode chamber. While this process was going on, electrolysis was occurring with the production of nitric acid about the anode and barium hydroxide about the cathode. In the course of time, the liquid from the immediate neighborhood of the anode, *rapidly becoming distinctly acid,* was carried into the diaphragm by endosmose. The charge on the diaphragm finally reversed, passing through zero to a positive value, while the direction of the flow changed to the anode. Had Holmes continued still further he would have observed a *second* reversal, for in time the alkaline liquid from the cathode would have been drawn into the diaphragm, would have neutralized the acid, and finally would have changed the sign of the electrification from plus to minus. These reversals could be kept up as long as one wished; the frequency of their occurrence would depend upon the thick-

ness of the porous walls and their proximity to the electrodes, the area of which would have to be fairly large.

Mr. Pierson was good enough to test this point for me in my laboratory in Worcester. He employed a specially constructed electro-osmometer to be described later and used a carborundum diaphragm. Dilute neutral solutions of the alkali chlorides between platinum electrodes acted in the manner outlined in the preceding paragraph and successive reversals were obtained.

Coehn[1] has worked with a Pukall filter. Solutions of potassium hydroxide and sulphuric acid always went to the cathode. Nitric acid went to the anode when more concentrated than one milligram-molecule to the liter, while acetic acid did not show reversal until 200 milligram-molecules had been exceeded. These numbers represent the composition of the liquid phase at the isoelectric point. Neutral sulphate solutions flowed to the cathode under all circumstances and alkali nitrate did the same. But solutions of the heavy metal nitrates flowed to the anode, except when extremely dilute.

Barratt and Harris[2] have worked with diaphragms of gelatine, agar, and parchment. The authors report the usual acid-alkali reversal with gelatine (also reported by Perrin); but, with agar and parchment, a flow to the cathode occurred even in acid solutions. This behavior is not surprising in the case of parchment in view of what Perrin found with cellulose but the failure to show reversal is somewhat puzzling in the other case, more especially when one considers the similarity between agar and gelatine. As a matter of record, some of my own experiments have shown that traces of acid do reverse the flow through an agar diaphragm.

With a diaphragm of ten percent gelatine, solutions of Na_2SO_4, NaOH and $NaNO_3$ flowed to the cathode in the following order: $Na_2SO_4 > NaOH > NaNO_3$ (slowest), *and the rate for a given solute increased with the concentration.* Solu-

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[1] Wied. Ann., **64,** 227 (1898); Zeit. Elektrochemie, **16,** 586 (1910).
[2] Zeit. Elektrochemie, **18,** 221 (1912).

tions of HNO_3, $Cu(NO_3)_2$ and $Al(NO_3)_3$ flowed to the anode in the order $Al(NO_3)_3 > Cu(NO_3)_2 > HNO_3$ (slowest). With parchment the solution always flowed to the cathode, the order being: $Na_2HPO_4 > Na_2SO_4 > NaOH > NaCl > HCl > CuCl_2 > AlCl_3$ (slowest). In the particular cases of the copper and aluminum chlorides the rate of flow rose to a slight maximum with increasing concentration but soon fell almost to zero even when the amount of salt present was actually very small.

With agar diaphragms, as the concentration of dissolved electrolyte increased, the endosmose passed through a distinct maximum in every instance. As in the previous case, the rate of flow (always toward the cathode), decreased in the following order: $Na_2HPO_4 > Na_2SO_4 > NaOH > NaCl > HCl > CuCl_2 > AlCl_3$. Barratt and Harris would have obtained more interesting data, no doubt, if they had followed Perrin's method of working always in acid or alkaline solutions. It would be interesting to work out the influence of the Hofmeister series. My guess is that the order of the series will be reversed, when the salts are used in acid instead of alkaline solutions.

An elaborate study of electric endosmose in neutral solutions has been completed recently by Elissafoff[1] in Freundlich's laboratory. His procedure was based on Lemström's[2] method of measuring endosmotic movements in a single capillary without the direct application of electrodes. A horizontal capillary of glass or quartz was held between the charged poles of an influence machine, with the axis of the tube parallel to the lines of force in the electric field. The capillary was filled with liquid except for a small bubble of air; on the application of the external electric field, a film of liquid was dragged along the surface of the glass and around the air bubble, until a drop collected finally at one end or the other of the tube. This form of apparatus has obvious advantages and disadvantages, among the latter being the limited number of materials that are available for study and the

[1] Zeit. phys. Chem., **79**, 385 (1912).

[2] Drude's Ann., **5**, 729 (1901).

relatively small interfacial area. The actual transport of liquid was very small.

By comparing solutions with pure water, Elissafoff arrived at the following empirical relation between endosmose and composition:

$$\Delta V_e{}^- = R \log_e C + \gamma$$

where $\Delta V_e{}^-$ is the *lowering of endosmose* by adding the salt to water, C is the concentration of the solution and R and γ are constants.

In the following table some of Élissafoff's data are reproduced, the numbers under "half-value" referring to the concentration of solutions which have a rate of endosmose one-half that of pure water.

I. GLASS CAPILLARY (NEGATIVE AGAINST DISTILLED WATER)

Substance in solution	Half-value
NaCl	260 millimols/liter
$^1/_2$ K$_2$SO$_4$	270
Morphine hydrochloride	51
AgNO$_3$	47
Neufuchsin	41
HNO$_3$	39
BaCl$_2$	37
UO$_2$(NO$_3$)$_2$	35
Potass. benzoate	29
Ce(NO$_3$)$_3$	8.6
$^1/_2$ Al$_2$(SO$_4$)$_3$	4.5
HgCl$_2$	3.8
Th(NO$_3$)$_4$	2.7

II. QUARTZ CAPILLARY (NEGATIVE AGAINST DISTILLED WATER)

Substance in solution	Half-value
Sod. picrate	220–400
KNO$_3$	140 millimol/liter
Picric acid	100 approx.
HNO$_3$	46
CaCl$_2$	26
Th(NO$_3$)$_4$	0.44
$^1/_2$ Al$_2$(SO$_4$)$_3$	0.24

These data show that Perrin's rules hold to a certain extent. Both glass and quartz are strongly electronegative and are affected by the cations in most cases. So far as the alkali and light metal salts are concerned the Perrin-Schulze valency rule holds without exception, but when we come to the heavy metals and certain organic cations the valency rule fails completely. The organic cations specified are univalent, yet they appear quite as effective in neutralizing the negative charge on the capillary walls as the divalent light metal cations. Silver falls in with the divalent light metals; mercuric chloride is as effective as aluminum sulphate. Potassium benzoate and sodium picrate give odd results.

No reversal by acids was observed, but the strength of the solutions employed was never greater than one ten-thousandth normal. With certain salts, however, reversals were obtained. Against solutions of thorium nitrate of sufficiently high concentration the glass or quartz became electropositive and a similar reversal occurred with solutions of methyl violet, a basic dye. One should compare this with what Larguier des Bancels found with wool and basic dyes.

In all of these cases, addition of electrolyte produced a decrease in the rate of endosmose. On the other hand potassium hydroxide solutions *increased* the flow toward the cathode. There seems to be, accordingly, no hard and fast rule that dissolved substances always reduce the contact electrification, just as there is no relation holding rigidly between valence and lowering of the contact potential or between valence and coagulation. Neither the empirical formula of Elissafoff nor the rules of Schulze and Perrin are more than working hypotheses applicable to special cases.

Very recently some experiments have been described by Byers[1] who worked both with tripartite cells and with an apparatus containing as many as five porous earthenware diaphragms. The procedure employed in measuring the endosmose was exceedingly unsatisfactory and the data published are of doubtful value, as they are rough approxima-

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[1] Jour. Am. Chem. Soc., **36**, 2284 (1914).

tions only. Neither the fall in potential through the diaphragm nor the current was held constant, so that anything but indirect comparison was out of the question. Similar results were published years ago by Napier,[1] in whose experiments Byers seems to have been able to introduce little improvement. A discussion of Byer's results will be undertaken later.

Various attempts have been made from time to time to apply electrical endosmose to practical purposes. Not the least interesting of these is electrical tannage,[2] which has been employed occasionally for many years, though never with any real success.

Some interesting experiments have been described by Roever[3] who investigated tanning with a direct current, using dilute quebracho extract and a raw-hide diaphragm. He found that the infiltration of the raw liquor into the hide was greatly accelerated by the electric current. The direction of flow through the hide was from anode to cathode, and the amount of liquid transported was directly proportional to the applied E. M. F. With 100 volts fall in potential through the hide-diaphragm, the total quantity of liquor pumped amounted to 7.38 kg. per hour for each square meter of hide surface.

More recently the problem of electric tannage has been discussed by Rideal and Evans[4] and also by Williams.[5] Williams observed quite correctly that the failure of electrical tannage is caused by decomposition of the tannins at the electrodes by electrolysis. He therefore recommended electrical endosmose with an *alternating* current, to prevent decomposition of the tan liquid. It seems obvious, of course, that an alternating current cannot produce a steady electro-osmotic flow in one direction, so that Williams suggestion

[1] Phil. Mag., (3) **29,** 16 (1846).
[2] Folsing: Zeit. Elektrochemie, **2,** 167 (1893); Rideal and Trotter: Jour. Soc. Chem. Ind., **10,** 425 (1891).
[3] Wied. Ann., **57,** 397 (1896).
[4] Jour. Soc. Chem. Ind., **32,** 633 (1913).
[5] Jour. Am. Leather Chemists Assoc., **8,** 328 (1913).

appears to be based on a misconception. In this connection Professor Bancroft has suggested to me that the accelerating action of the alternating current may be due to electric heating and consequently increased diffusion.

Rideal's experiments were rather involved and the conditions were not kept at all constant. They consisted essentially in watching the passage of tan liquor through a diaphragm of gelatine under the influence of a low E. M. F. (not over 10 volts), the gelatine containing ferric chloride as indicator. No allowance was made for the ionic migration of the indicator or for the complicating circumstances that its use introduced. The movement of the tan liquor into the gelatine occurred in both directions, but most rapidly toward the anode. This, according to Rideal, represented ionic migration of the tannic acid anion, the less noticeable flow to the *cathode* being that produced by electrical endosmose. The correctness of these conclusions is anything but certain and Rideal's experiments should be repeated.

, The possibility of removing water from spongy or suspended material by electro-osmosis has been considered in some detail in Germany. The peat bogs of the latter country and of Ireland offer a very great potential source of fuel, if only a sufficiently economical method of removing the water from the material can be devised. Dried by steam, the peat produced is balanced by the coal consumed. Accordingly methods have been devised by von Schwerin, in particular, to remove the water from a mud of ground-up peat, by a process which is really a combination of electrical endosmose and cataphoresis.

In an address before the Bunsen Society von Schwerin[1] has discussed his process, illustrating it by removing water from alizarin paste and ground-up peat. The suspended solid tends to migrate toward one electrode by cataphoresis while the water flows in the opposite direction by electrical endosmose and is removed. The many forms of apparatus do not interest us here. From a peat mixture containing originally 85 to

[1] Zeit. Elektrochemie, 9, 739 (1903).

90 percent of water, it is claimed that three-quarters of the water can be removed, at a cost of only one-fifth of the energy available from the recovered peat. The most suitable potential gradient through the peat mixture is stated to be 4 or 5 volts per centimeter and from 13 to 15 kilowatt-hours are required to remove a cubic meter of water. The process does not seem to be a great success at present, however, doubtless owing to the difficulty of removing the remaining one-quarter of the water.

Nernst[1] has discussed the principle underlying von Schwerin's process and with Brill has observed what seems obvious—that one is dealing not with a case of true desiccation but merely with a mechanical removal of water. Electrical endosmose does not lower the partial pressure of water vapor over the liquid, and true drying does not occur.

In view of the first of Perrin's rules, it is most significant that in the German patent No. 233,281 (1910), von Schwerin recommends the addition of acids "to those substances which wander to the cathode" (positively charged substances) and the "addition of alkali to the paste of those substances which migrate to the anode." It is obvious that the process should be accelerated, provided that one avoids certain polyvalent anions in the one case and certain polyvalent cations in the other.

In diaphragm electrolysis[2] (of the alkali chlorides for example) the phenomenon of electrical endosmose may come into play. The consideration of this case has been undertaken by Tardy and Guye,[3] whose original paper may be consulted for details. ·

Contact Electrification and Adsorption

The earlier attempts to explain electro-osmose are interesting. Wiedemann believed that the electric current exerted a tractive action upon the liquid in a capillary tube

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[1] Verh. Deutsch phys. Ges., **11, 112** (1909).

[2] Bancroft: Trans. Am. Electrochem. Soc., **3,** 261 (1903).

[3] Jour. Chim. phys., **2,** 115 (1904).

and that the liquid was carried thus from anode to cathode, regardless of the substance composing the walls. In opposition to this view, Graham,[1] Quintus Icilius, and Breda and Logemann,[2] showed conclusively that no transport of liquid occurred unless a diaphragm or its equivalent were present. As I observed in the earlier pages of this paper, we owe to Quincke and to Helmholtz the electrical double layer theory of contact electrification. The Coehn rule is an interesting development of this theory. But both Quincke and Helmholtz contributed little to further our understanding of why and how an electrical double layer or its equivalent may be formed when solid and liquid are placed in contact.

For the special case of a metal in contact with its own ions in solution the Nernst theory holds. It is only natural that there should have been proposed an analogous explanation of the contact potentials of non-metallic solids. Every solid dissolves in water to a certain extent and the electrical double layer might be supposed to be produced by differences in the rates of ion diffusion—if the cation diffused faster, a separation of charges would tend to occur and the solid (or liquid immediately in contact with the solid) would become negative. Bredig[3] has given vague expression to this idea by observing that the Coehn rule points to some relation between the solubility of ions in different media and the dielectric constant.

As a matter of fact, the explanation outlined above cannot be the correct one for the case of a solid immersed in a pure liquid, unless one postulates that the liquid remains unsaturated with respect to the solid or that fresh liquid is being supplied constantly. The electrical charge does not disappear when the liquid is saturated with the particular solid, although its sign and intensity may change, while the potential difference at the liquid interface in a concentration cell exists only so long as a difference in concentration is maintained. No

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[1] Phil. Mag., (4) **8**, 151 (1854).
[2] Pogg. Ann., **100**, 149 (1857).
·, [3] Zeit. Elektrochemie, **9**, 738 (1903).

permanent potential difference can possibly be produced as the result of unequal ion mobilities. We shall see that adsorption offers a rational explanation.

The contact potential between a solid and a solution is a more complex problem. Perrin has offered an explanation of his acid-alkali rule by postulating that, since hydrogen and hydroxyl ions are abnormally mobile, they are correspondingly small, and are able thereby to crowd to the surface of a solid more closely than the other ions. This might account for the solid being positive in acid and negative in alkaline solutions.

Now, this "crowding to the surface" postulated by Perrin is nothing more than selective adsorption and it becomes a simple matter to include this hypothesis with the adsorption theory. To what extent selective adsorption depends upon the relative mobilities of the ions is quite another story, although the work of Holmes and Frazer seems to indicate a relationship in case the ions are very similar chemically. In this connection Rutherford[1] passed an ionized gas through a narrow metallic tube and found that the latter became electrified positively or negatively according to the sign of the charge on the more rapidly diffusing (hence the smallest) ion.

Perrin himself was unable to reconcile his theory with all the facts, for he observed that lithium bromide failed to charge a chromic chloride diaphragm negatively although bromine ions are twice as mobile as lithium ions. The difficulty, however, is not so great as it appears, for Perrin neglected to take into account the ions produced in the solution by the dissolving chromium chloride. My guess is that, if some relation does hold between selective adsorption and ion mobilities, the tendency to reduce the positive charge on chromic chloride will be greater with lithium bromide than with potassium bromide for instance. The data of Fraser and Holmes confirm this to a certain extent.

Haber[2] has suggested for the particular case of glass against

[1] See Cameron and Oettinger: Phil. Mag., (6) **18**, 586 (1909).
[2] Haber and Klemensiewicz: Zeit. phys. Chem., **67**, 413 (1909).

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water that the solid is essentially a hydrogen electrode, and that the magnitude of the potential difference depends upon the concentration of hydrogen ions in solution. Guided by Haber's theory Cameron and Oettinger[1] performed some rather inconclusive experiments on the E. M. F. produced by acid and alkaline solutions forced through a capillary of glass. Haber's theory, as Freundlich points out, is open to the serious objection that electrical endosmose does not depend entirely upon hydrolysis of the dissolved solute, as it should do if the concentration of hydrogen ions is the only factor. Acidity and alkalinity, while of very great influence, are not the only factors determining electro-osmotic effects.

Freundlich[2] was the first to point out clearly the intimate relations existing between adsorption and electrical endosmose. This development may be said to be the result of his own work on adsorption and the speculations of Perrin[3] regarding the analogies between the behavior of suspensions and the peculiarities of electrical endosmose. Freundlich went still farther than Perrin. He had already shown the relation between adsorption· and the stability of suspensions and had pointed out the validity of the Schulze valence rule for adsorbed light-metal cations and the ordinary anions. He had discovered, too, that many organic ions as well as the heavy metal cations were exceptions to the Schulze rule. He was able, as a result, to emphasize the similarity between the Schulze rule and the valence rule of Perrin, and, from Elissafoff's data, he showed that exceptions to Schulze's rule were exceptions likewise to Perrin's. From this it was only a step forward to apply to electro-osmotic phenomena a definite theory based upon adsorption, or more specifically, upon the selective or preferential adsorption of ions.

Freundlich called the difference of potential between solid and solution, the "adsorption potential." If a cation is adsorbed to a greater extent than the accompanying anion,

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[1] Phil. Mag., (6) **18**, 586 (1909).

[2] Kapillarchemie, 245 (1909); Zeit. phys. Chem., **79**, 407 (1912).

[3] Jour. Chim. phys., **3**, 85 (1905).

the solid becomes positively charged, and if it is employed as a diaphragm, the electrical endosmose will occur from cathode to anode. For the case of a solid against pure water it is only necessary to postulate selective adsorption, either of the ions already present in water or produced by the solid dissolving. When preferential ion adsorption occurs, the number of ions actually adsorbed is very small, because the charge on a single ion is relatively large and the electrical double layer that is established opposes any further spacial separation of positive and negative ions.

Freundlich[1] has recently modified his original theory of the adsorption potential, without improving matters appreciably and not without adding several complicating hypotheses. He postulates that the contact potential of the diaphragm depends upon the nature of the material of which it is composed (upon differences in solution tension of the ions thrown out) and that it is affected only indirectly by adsorption. In my opinion contact potential does undoubtedly depend upon the nature of the solid itself, but the important thing is the power of the solid to adsorb selectively the ions present in the liquid from the beginning, or produced by the solid dissolving.

Frazer and Holmes,[2] following a suggestion rejected by Whetham,[3] have advanced a distinctly different hypothesis based upon the solvate theory. If the hydration of the cation is greater than that of the anion, for example, liquid should be carried from anode to cathode; and this is what the authors found to be the case with neutral salts of the alkalies against earthenware. Since the mobility of an ion may be regarded as an inverse measure of its hydration, one should expect a strong flow to the cathode in an alkaline solution and a strong flow to the anode in an acid solution. This deduction agreed with the facts as far as they were determined by Frazer and Holmes. Furthermore, in a given series of salts with a

[1] Freundlich and Elissafoff: Zeit. phys. Chem., **79**, 407 (1912).
[2] Am. Chem. Jour., **40**, 319 (1908).
[3] "Theory of Solution," 292 (1902).

common anion, the amount of flow to the cathode should increase with decreasing ionic mobility. Holmes confirmed this experimentally with the alkali nitrates.

Barratt and Harris have discussed a similar theory[1] which I shall give in the words of the original:

"The flow of liquid in electro-osmose is obviously determined by the movement of the ions contained in the liquid at the surface of contact with the solid. These ions, as they move under the influence of the potential gradient, cause a passive movement, in the same direction, of the molecules of the liquid. The narrower the interval between the particles of which the diaphragm is composed, the more marked this movement of liquid will be. Further, the more numerous the ions in the liquid portion of the double layer, the greater the flow of liquid will at first be, though with continued increase in number of ions a diminution of concentration of fluid will later occur and the flow will diminish; thus the curve obtained by plotting concentrations as abscissas against rates of flow, as ordinates, will exhibit a maximum, ...

"Up to the present it has been tacitly assumed that electrical endosmose has been brought about solely by the movement of unaltered ions. If, however, the ions in question become centers for the condensation or combination of water molecules, then an additional factor in the transport of fluid would come into play."

Barratt and Harris postulate further that the electric current will be carried through the diaphragm by those ions not in the double layer and if these are hydrated the flow of liquid will be greater by a certain amount, which will depend upon the relative hydration of anion and cation and their transport numbers. Nevertheless, they were not quite sure of the rôle played by hydration, for they found, in the case of agar diaphragms, from 18 to 370 molecules of water transported through the diaphragm for every molecule decomposed electrochemically—"a circumstance which may be interpreted as indicating that conveyance of fluid by hydrated

[1] Biochem. Jour., 6, 315 (1912).

ions plays only a subordinate part in electro-osmose." Some of my own experiments confirm this statement; for, with a current of less than two milliamperes, I have caused several grams of water to flow through an a'undum diaphragm in one minute. To account for this one must assume the ion hydration to be extremely great.

The theory of Frazer and Holmes cannot be correct, for one would have to conclude, in consequence, that there is a fundamental difference between electrical endosmose and Quincke's diaphragm currents. Moreover the theory assigns to the diaphragm a subordinate and purely mechanical rôle. Neither does it explain why mere traces of lanthanum salts, for instance, reduce the flow of an alkaline solution, or why an acid solution *flows to the cathode* through powdered glass. If there is any relation between endosmose and ion mobility, it is better to consider it an indirect one, produced by a possible relation between ion mobility and ion adsorption, as I pointed out when discussing Perrin's speculations.

Having considered the facts, so far as they are known, together with the different theories regarding electrical endosmose, I am of the opinion that the most satisfactory working hypothesis is the one proposed originally by Freundlich and emphasized more recently by Bancroft[1] in the following words:

"The sign of the charge on a diaphragm depends upon the relative adsorption of cation and anion, being positive if the cation is adsorbed to a greater extent than the anion and negative if the reverse is the case."

We start with the properties of surfaces. By virtue of these properties solids are able to adsorb substances from a liquid with which they are in contact. They may adsorb a particular ion preferentially, in which case we have selective ion adsorption and either a positive or negative charge on the solid. The adsorbing substance tends to be peptized by the adsorbed ion. Or solids may adsorb the solvent itself and be peptized, while the other possibilities, all of which tend to

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[1] Jour. Phys. Chem., **16**, 312 (1912); Trans. Am. Electrochem. Soc., **21**, 233 (1912).

produce peptization, are adsorption of a non-electrolyte, an undissociated salt, or a second colloid.[1] Since electrical endosmose has to do with electrically charged surfaces, we are concerned chiefly with preferential adsorption of ions.

We postulate that every solid has a specific adsorbing power for a given ion, which depends upon the specific surface[2] of the solid, upon the temperature, upon the concentration of the particular ion in the solution and upon the other ions present, or adsorbed previously by the solid. When the ion content of a liquid is vanishingly small, we shall have but little ion adsorption and little electrical endosmose. Nondissociated and non-dissociating liquids show little electrical endosmose (Perrin, Coehn), an experimental confirmation of the preceding statement. On the other hand "pure" water shows marked endosmose through many solids. This is a case of preferential ion adsorption where the ions are produced both from the ionization of water itself and the solution of the solid, which we shall see is a very important matter in some cases (notably glass). Now, since the majority of solids are negative against water, we postulate that hydroxyl ions are usually adsorbed in preference to hydrogen ions. Freshly precipitated alumina is reported to be electro-positive; my idea regarding this is not that alumina on dissolving sends out rapidly diffusing hydroxyl ions and becomes positive against the solution, but that it adsorbs aluminum or hydrogen ions more easily than hydroxyl ions. Crystalline alumina in the form of alundum is electro-negative against water, and in this respect shows a distinct difference as compared with the gelatinous form, a difference which may be due, not only to the alteration of its surface by agglomeration, but also to its slower rate of solution. In discussing the potential of a solid against water *originally pure*, we must accordingly take two factors into account:

(1) The specific adsorption capacity of the solid for

[1] Cf. Bancroft: Jour. Phys. Chem., **20**, 85 (1916).
[2] Wo. Ostwald: Grundriss der Kolloidchemie, 29 (1912).

hydrogen and hydroxyl ions produced by the dissociation of water.

(2) The solution of the solid, which, though extremely small in many cases, may produce ions that are strongly adsorbed.

Hydrogen ions are often adsorbed preferentially from solutions containing them, especially from acids, though we have seen that the rule is by no means a general one. My experiments have shown that alumina, which is positive in dilute hydrochloric acid, is weakly negative in citric acid where the equivalent selective adsorption of the citrate ion must be greater than that of the hydrogen ion. Moreover we know that metal sulphides are peptized by hydrogen sulphide, an acid, yet the adsorbed ion is sulphur and not hydrogen; the particles in suspension are electro-negative.[1]

In general the same statement applies to the adsorption of hydroxyl ions. Solids seem to have a somewhat greater adsorption affinity for hydroxyl ions than for hydrogen ions, though there are notable exceptions to this generalization. The general theory covering the electrical endosmose of all liquids and solutions may be formulated as follows:

(1) Electrical endosmose depends upon the preferential or selective adsorption of ions and is influenced only by those ions which are adsorbed by the diaphragm.

(2) Any circumstance or condition wh ch changes the adsorption produces an effect upon electrical endosmose. Electrical endosmose varies, therefore, with the condition of the surface (for a given solid), with the relative and absolute ion concentrations, with the temperature and so forth.

(3) The *direction* of endosmose indicates the sign of the diaphragm; the *rate* of endosmose is proportional to the intensity of the charge on the diaphragm in case the potential gradient through the diaphragm is constant. When the liquid flows to the cathode, the diaphragm is negative; when it

[1] Winssinger: Bull. Soc. chim. Paris, (3) **49,** 452 (1888); Linder and Picton: Jour. Chem. Soc., **61,** 116 (1892).

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flows to the anode the diaphragm is positive. No flow at all indicates an isoelectric condition.

(4) A diaphragm tends to become positive by the selective adsorption of cations, and negative by the adsorption of anions.

(5) The positive charge produced by an adsorbed cation is neutralized more or less by the addition of an adsorbed anion, the effect increasing with the concentration of the anion. Similarly, the negative charge produced by an anion is neutralized by an adsorbed cation.

(6) Electrical endosmose measures the tendency of a solid to form an electrical suspension in a given liquid but it does not measure the tendency of the solid to form a non-electrical suspension, such as is produced by adsorbed solvent, solute or neutral colloid.

One of the most beautiful cases illustrating the theory is afforded by the experiments of Lottermoser[1] on the halides of silver. It was shown that these halides are peptized in suspension by silver or halogen ions, while nitrate and alkali metal ions are of little influence. Silver chloride, for example, is peptized strongly by a slight excess of either silver or chlorine ions and, accordingly must adsorb those ions preferentially. In the light of the adsorption theory of electrical endosmose, silver chloride peptized by silver ions should be positively charged, but negatively charged when peptized by chlorine ions. Such was actually the case. Although Lottermoser did not study electrical endosmose with silver chloride diaphragms, he did show that cataphoresis occurred in the expected direction in both cases.

By applying the adsorption theory and making certain assumptions that accord with previous and later experiments Bancroft was able to explain some curious phenomena observed by Reed[2] with tripartite cells. By assuming that the selective adsorption from solutions of equal concentration varies according to the series $H^{\cdot} > SO_4^{\cdot\prime} > Cu^{\cdot\cdot} > NO_3^{\prime}$ one is

[1] Jour. prakt. Chem., (2) **72**, 53 (1905).
[2] Trans. Am. Electrochem. Soc., **2**, 238 (1902).

able to understand why acid (and neutral) solutions of copper nitrate flow to the anode through a porous cup while solutions of copper sulphate flow in the opposite direction.

Byers and Walters[1] have recently made a study of "electrolytic" endosmose in cells containing several diaphragms. In their first experiments with three-compartment cells they confirmed the earlier experiments of Parker,[2] without being impressed with the surprisingly correct explanation of affairs that Parker offered.

Their apparatus consisted essentially of a large vessel containing two porous cups, in one of which was placed a large platinum anode while the other contained the cathode. On filling the whole system with a solution of potassium permanganate, acid and alkali were produced in the anode and cathode compartments, respectively, and both cups were observed to fill up by electrical endosmose. Byers was puzzled by this occurrence and concluded that endosmose is "capable of producing flow of electrolytes . in both directions at the same time."

What Byers has forgotten is that he was dealing with two diaphragms. If we postulate that both diaphragms adsorb hydrogen or hydroxyl, as ion, more than they do potassium or permanganate, the porous cup enclosing the anode should become positive and the other, enclosing the cathode, negative. A flow *into* both cups should result, since the endosmose will be from cathode to anode through the anode cup and from anode to cathode through the cathode cup. Everything is perfectly intel igible.

Parker, discussing the phenomenon of simultaneous endosmose in opposite directions, wrote as follows:

"To account for this we must assume that *ions* also affect the character of the charge of the contained liquid in respect to the walls of the cell. If this be the case we have an explanation for this phenomenon since in the alkali cups the ions

[1] Jour. Am. Chem. Soc., **36**, 2284 (1914).
[2] Johns Hopkins Dissertations, **31**, 23 (1901).

potassium and hydroxyl, and in the acid cups the ions H and MnO$_4$ were present."

Much of Byers' work can be accounted for by the theory. There are some puzzling things that will need explaining, but until the experiments have been repeated they should not be regarded as conclusive, as it is only too apparent that no rational procedure was adopted. The strength of the solutions was varied in a haphazard fashion and the potential gradient was never twice the same. Byers seems to have been unfortunate regarding his views on the direction of endosmose, as I shall show by quoting from the original:

"In the experiments with ferric chloride, uniform results are secured and only anodic flow is noted. Yet the flow *from* the cathode cup is so marked that to keep from disconnecting the current solution must be added. In Expt. 19, 220 cc were added to the cathode while only 20 cc passed into the anode cup. Manganese chloride and magnesium chloride also show only negative flow, and *from* the cathode cup in excess of that *into* the anode cup........"

What Byers means is that a solution of ferric chloride flowed through both diaphragms from cathode to anode and that the same occurred with manganese and magnesium chlorides. Why the rates of flow showed such differences is a question—possibly the condition of the porous walls or the potential gradient were different in the two cases. Furthermore the direction of the flow (to the anode through both cups) was what one would expect with a weakly negative diaphragm and a strongly adsorbed cation which follows Schulze's rule. On repeating the experiment with a six-compartment cell and five diaphragms, Byers again obtained a flow to the anode with ferric chloride solution.

In passing, I wish to point out that ferric chloride solutions belong to a class which should be avoided, wherever possible, in experiments upon electrical endosmose, sensitive as this phenomenon is to minute quantities of adsorbable material. One has to consider in this case the iron, chloride, and hydrogen ions, as well as the hydrous iron oxide in suspension.

These experiments of Byers are instructive, for, aside from being the latest work in the field, they emphasize the obscurity still surrounding electrical endosmose and the necessity for carefully redetermining the facts.

The chief points brought out by this paper may be summarized as follows:

(1) The development of our present knowledge regarding electrical endosmose has been outlined and especial emphasis has been laid on the electro-osmotic behavior of solutions.

(2) The different theories of electrical endosmose have been discussed critically.

(3) The most satisfactory of these is the Freundlich-Bancroft adsorption theory which agrees with the facts whenever these are accurately known.

(4) A new and convenient apparatus for studying electrical endosmose, together with the experimental data obtained, will form the subject of a separate paper.

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ELECTROLYTIC FORMATION OF PERCHLORATE

BY E. L. MACK

The usual conception of the mechanism involved in the anodic formation of perchlorates from chlorates is largely due to Oechsli[1] and his theory has gradually found its way into the text-books of electrochemistry with the result that it is at the present time commonly accepted as representing the actual mechanism of the process.

According to this theory the reaction at the anode during chlorate electrolysis is not to be considered a direct addition of oxygen to ClO_3' with the formation of ClO_4' but rather as a more complicated process, during which we must suppose the liberation of the chlorate ion. Briefly, the various steps involved are as follows: Chlorate ion is liberated by the current and, assuming that it acts in a manner analogous to other strongly acid anions, reacts with water at the anode with the formation of free chloric acid and liberation of oxygen,

$$2ClO_3 + H_2O = 2HClO_3 + O. \qquad (1)$$

The free chloric acid generated in this way is probably at a very high concentration in the film of electrolyte which is in immediate contact with the anode. Since in this condition it is known to be very instable, spontaneous decomposition takes place, perchloric and chlorous acids being formed,

$$2HClO_3 = HClO_4 + HClO_2. \qquad (2)$$

The free chlorous acid thus formed very evidently cannot remain in the solution as such, since in contact with the chloric acid present it would immediately evolve chlorine dioxide:

$$HClO_3 + HClO_2 = H_2O + ClO_2 \qquad (3)$$
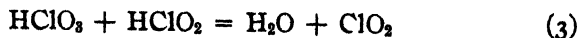
This evolution of chlorine dioxide has never been observed to take place during this process, and the theory, therefore, assumes that the chlorous acid formed as shown in (2) is immediately oxidized to chloric acid by the oxygen from the

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[1] Zeit. Elektrochemie, **9**, 807 (1903).

decomposition of water by the liberated ClO_3' ions, as shown in (1).

The sum total of the reactions which, according to this theory, takes place at the anode may then be represented by:

$$2ClO_3' + H_2O + 2F = HClO_4 + HClO_3$$
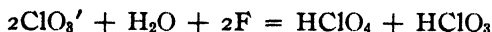
Oechsli, in order to satisfactorily explain the formation of perchlorate, finds it necessary to assume the liberation of the chlorate ion mainly for the following reasons: Oxygen when discharged under conditions such that the electrode is reversible probably requires a lower voltage-than that needed for the liberation of oxy-acid anions,[1] but if we deal with an electrode which is not reversible toward oxygen, that is, where the discharge of oxygen requires a considerable overvoltage, a point may be reached at which the discharge of the oxy-acid anion will become easier, or require a lower voltage, than that for oxygen and will consequently take place. From this standpoint, assuming that ClO_3' is discharged, the formation of perchlorate could be expected to take place only at an anode where the overvoltage for oxygen liberation is sufficient to allow the preferential discharge of the chlorate ion. It is held that this hypothesis is supported by the following facts: (1) Perchlorate formation goes on with a markedly higher efficiency at a smooth platinum anode, where oxygen overvoltage is known to be high, than at an anode of platinized platinum, where oxygen discharge takes place much more easily. (2) If the solution is made alkaline at the anode the efficiency of perchlorate production falls off rapidly; a fact which is explained by the increased ease of oxygen discharge in a solution containing a high concentration of hydroxyl ions. The result is a discharge of oxygen along with the chlorate ions and a consequent drop in the anode efficiency. (3) This hypothesis best explains the rise from a comparatively low efficiency at the beginning of the electrolysis to a higher value as the electrolysis proceeds. When the oxidation is taking place at a high efficiency and the current is interrupted for a

[1] Bose: Zeit. Elektrochemie, **5**, 169 (1898).

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short time, it is found, upon closing the circuit, that the effi-
ciency is low just as it was during the first few minutes of the
experiment. The idea is that during the break in the current
flow the concentration of free chloric acid at the anode falls,
largely through diffusion, and that a certain length of time is
necessary for the chloric acid to accumulate to that concen-
tration in which it is unstable. During this time oxygen is
evolved and the current efficiency necessarily falls. (4)
Changing from a smooth platinum anode to one of platinized
platinum brings about a marked decrease in efficiency and this
is best explained by considering it equivalent to a decrease
in current density because of the larger surface presented by
the platinized electrode. At this lower current density the
efficiency must be lower because we would have more oxygen
liberated in proportion to the number of chlorate ions than
at the higher current density. Furthermore, many other
electro-chemical reactions which are commonly considered
as being due to anion liberation show this same characteristic
of decreased efficiency with platinized anodes. The formation
of persulphuric acid and Kolbe's[1] synthesis of ethane are cited
as being processes of this type. (5) An increase of tempera-
ture, at a fixed current density, brings about a decrease in
perchlorate formation and a corresponding increase in oxygen
discharge. This is considered to be the result of increase in
hydroxyl ion concentration caused by the increased dissocia-
tion of water at the higher temperature. (6) Finally, per-
chlorate formation must be conditioned by chlorate ion dis-
charge since the reaction has not been duplicated chemically;
that is, chlorate has not been oxidized to perchlorate by chem-
ical oxidizing agents.

This theory is open to the objection that it rests upon
several assumptions which may or may not be true. We have
no direct evidence that chloric acid, when sufficiently con-
centrated, decomposes with the formation of perchloric and
chlorous acids. The visible products of the decomposition
are known to be perchloric acid, chlorine dioxide, chlorine

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[1] Liebig's Ann., **69,** 257 (1849).

and oxygen. While the intermediate formation of chlorous acid is possible it has not, up to this time, been demonstrated satisfactorily. If we are to reason from analogy to the reaction which takes place when alkali chlorates are heated[1] it would appear much more probable that the primary decomposition products would be perchloric and hydrochloric acids.

Granting, however, that the liberated chlorate ion and free chloric acids would act in the manner assumed, the theory is still unsatisfactory in that it does not explain the decrease in yield of perchlorate on substitution of platinized for smooth platinum anodes or the marked fall in efficiency with rising temperature. In the former case, using a platinum anode a current efficiency of 97.0 percent was noted,[2] while with a platinized anode, the other conditions remaining unchanged, the efficiency dropped to 2.7 percent. It is very evident that it would be necessary to assume a tremendous decrease in current density to account for the marked efficiency drop at the platinized anode since a succeeding experiment shows that, under like conditions, using a smooth platinum anode and a current density approximately one-fourth that in the first experiment cited, the efficiency fell only to 92.0 percent.

Regarding the temperature effect it may be stated with certainty that the increase in the dissociation of water with a temperature rise of 73° is insufficient to account for a decrease in efficiency of 97 percent. The efficiency at 7° is 97 percent while no perchlorate is formed at 80° C, other conditions remaining unchanged.

It has seemed advisable, therefore, to postulate that the electrolytic formation of perchlorate does not depend upon the liberation of the chlorate ion but rather is to be considered as a direct addition of oxygen to the chlorate ion. The object of this paper is to show that the phenomena observed during perchlorate formation are most easily and satisfactorily accounted for from this viewpoint. It is further

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[1] Cf. Scobai: Zeit. phys. Chem., **44**, 319 (1903).

[2] Oechsli: Zeit. Elektrochemie, **9**, 812, 818 (1903).

proposed to furnish independent proof that chlorate may be
oxidized to perchlorate by strictly chemical means; that is,
under conditions where the liberation of chlorate ion cannot be
assumed.

Let us consider for a moment the conditions existing at
an insoluble anode during electrolysis of solutions containing
oxygen or hydroxyl ions. Recent investigations[1] have shown
that the action of the electrolyzing current is to liberate oxygen
in the active or atomic form. This oxygen unless depolarized
by some substance present at the anode will be converted
into molecular or gaseous oxygen, the reaction being repre-
sented by:

$$2O_1 = O_2$$
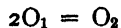
Further, it has been pointed out that the rate of this reaction,
and consequently the concentration of active oxygen or O_1,
which is present at the anode at any given time, is dependent
upon, (1) the nature of the anode material, (2) the current
density, (3) temperature, (4) nature of the solution, and (5)
the elapsed time of electrolysis.

Schoch[2] has pointed out that only an *exceedingly small*
voltage is required to discharge oxygen or any other ion into
an electrode which is absolutely free from electromotively
active material, and it follows from this and the above state-
ment that the potential of the anode, at any given time, in
a solution capable of discharging oxygen, depends primarily
upon the concentration of active oxygen then existent at the
electrode. Thus we see that by properly varying the condi-
tions we may have oxygen discharged at any potential above
a certain minimum value which is determined by the equilib-
rium value of the equation

$$2O_1 = O_2$$

at the particular anode and under the particular conditions
in question.

It may be well to point out here that in order to oxidize
a given substance present in the electrolyte, chlorate for

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[1] Bennett and Thompson: Trans. Am. Electrochem. Soc., **29**, 15 (1916).
[2] Jour. Phys. Chem., **14**, 665 (1910).

instance, it is necessary that the potential of the anode should rise *not to that point necessary to bring about the liberation of gaseous oxygen,* as is commonly believed, *but only to that point necessary to produce a concentration of active oxygen sufficient to oxidize the chlorate ion.* That this is the case and that the potential necessary for the latter process is very much less than that required for the former is conclusively shown by the work of Schoch.[1] Using a $N/3$ potassium chlorate solution and an iron anode it was found that the formation of perchlorate began when the anode potential reached +0.023 volt,[2] while a succeeding experiment showed that at an iron anode oxygen is not evolved until an anode potential of +1.5 volts is reached.

This experiment, even without the support of further evidence, shows that the formation of perchlorate is not determined by the liberation of chlorate ion since no one would claim for this ion a discharge potential as low as +0.023 volt. Most of the attempts at measurement have obtained values around +1.37 volts.[3]

Having thus shown that perchlorate can be produced at an anode potential far below that required for the liberation of oxygen as well as much below that commonly assigned for ClO_3' discharge, let us consider the phenomena actually observed during the electrolysis of a chlorate solution, assuming the formation of perchlorate to be the result of a direct addition of oxygen to the chlorate ion.

Using a smooth platinum anode in a strong neutral chlorate solution with a current density of, say, 4 to 6 amperes per square decimeter, we find the efficiency of perchlorate formation to be high, possibly as high as 95 percent. The anode potential is also found to be high and from the standpoint taken we consider that we now have at the anode active oxygen

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[1] Jour. Phys. Chem., **14**, 735 (1910).

[2] All potentials given in this paper are the observed readings against the normal calomel electrode. The signs are those observed in the experimental arrangement. This is in accord with the suggestion of Luther. See Le Blanc: Textbook of Electrochemistry, 4th Ed., 245.

[3] Le Blanc: Zeit. phys. Chem., **8**, 299 (1891).

in such concentration that it is able to oxidize the chlorate
ion rapidly and with good efficiency. We know that we are
here dealing with an anode which exhibits a high overvoltage.
This means that the concentration of active oxygen is above
the equilibrium value. If we decrease the current density
below the value first taken, we find a decrease in current effi-
ciency with respect to perchlorate formation and a corresponding
decrease in anode potential. This becomes intelligible when
we consider that at moderate current densities oxygen over-
voltage, and consequently concentration of active oxygen,
decreases[1] with decrease of current density. Again, if the
temperature be raised we find the current efficiency decreases
markedly. This, again, is in accord with the view taken since
we have seen that the concentration of active oxygen present
at the anode at any given time is dependent upon the state of
the reaction

$$2O_1 = O_2$$
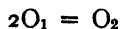
Increased temperature increases the velocity of this
reaction and tends to keep the concentration of active oxygen
down to the equilibrium value. We would expect, therefore,
a lower active oxygen concentration and consequently a lower
oxidizing power. A sufficiently high current density at the
higher temperature would, however, tend to increase the rate
of production of active oxygen and increase its concentration
in the electrode. As the current density is increased we should,
therefore, expect to obtain a consequent rise in efficiency of
chlorate oxidation tending to overcome the inhibitory effect
of the high temperature. This is actually realized experi-
mentally.[2] The current density used was 16 amperes per
square decimeter and with the solution maintained at 80°
gave a current efficiency of 13.5–14.8 percent. This was
raised to 40.0–42.5 percent when the current density was in-
creased to 20.8 amperes per square decimeter, the tempera-
ture remaining constant at 80°.

[1] Bennett and Thompson: Trans. Am. Electrochem. Soc., 29, 15 (1916).
[2] Oechsli: Zeit. Electrochemie, 9, 817 (1903).

If the solution is made alkaline the current efficiency falls off rapidly, a fact which is explained without difficulty when we recall that the discharge potential for oxygen at platinum is lower[1] in alkaline than in acid solutions. In other words, the active oxygen concentration is lower. Furthermore, oxidizing power in general is lower in alkaline than in neutral or acid solutions. This is to be concluded from the fact that many oxidations which take place readily in acid solution are either entirely prevented or proceed at a very much decreased rate when the solution is made alkaline.

It is noted that on starting the electrolysis both the potential of the anode and the efficiency are somewhat below their normal values. Both, however, steadily increase to a maximum with increasing time. This is entirely to be expected from the fact that reliable measurements of anodic overvoltage[2] always indicate a low concentration of active oxygen during the first few moments of oxygen discharge.

Finally, on substituting an anode of platinized platinum for one of polished platinum, other conditions remaining constant, we find a notable decrease in anodic efficiency. This, once more, is satisfactorily explained from our viewpoint, since the work of Coehn and Osaka[3] interpreted from the viewpoint which we have taken shows that at a given current density we must have a lower concentration of active oxygen at a platinized anode than at one of smooth platinum. Their results[4] gave for the potential of oxygen at smooth platinum $+1.39$ volts, and at platinized platinum $+1.19$ volts.

From what has been said above, it becomes evident that we can satisfactorily account for the anodic formation of perchlorate without assuming anything at all about the liberation of the chlorate ion, by considering that the oxidation is

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[1] Smale: Zeit. phys. Chem., **14**, 577 (1894).

[2] Foerster and Piguet: Zeit. Elektrochemie, **10**, 714 (1904).

[3] Zeit. anorg. Chem., **34**, 86 (1903).

[4] The measurements given by them were made against a normal hydrogen electrode but for the sake of consistency in this paper these have been converted to the normal calomel electrode values.

dependent only upon the presence at the anode of a sufficient concentration of active oxygen. It has been satisfactorily shown that this concentration corresponds to an anodic potential far below that required for liberation of gaseous oxygen and nearly as far below that required for the liberation of the chlorate ion, if we are to accept for this the values given by the best measurements available.

Although it may be readily admitted that the potential of the anode during the electrolysis of a chlorate solution is at all times probably above that necessary for chlorate discharge, it must be kept in mind that these reactions will not take place as long as we have chlorate present in sufficient concentration. This follows since it has been shown that the direct oxidation of the ClO_3' is the more easily accomplished process, that is, the one requiring the lowest potential and as such will take place first. This does not mean that the oxidation will take place under all conditions with high efficiency since we have seen that those factors which unfavorably affect this reaction are exactly those which tend to lower the concentration of active oxygen at the electrode. The direct result of this decrease is a decrease in its ability to oxidize chlorate and a corresponding increase in the ease of oxygen evolution and the consequent drop in current efficiency with respect to perchlorate formation.

Experimental

Although the theory outlined above is well supported by known facts, it has seemed desirable to have independent proof of the fact that chlorates may be directly oxidized to perchlorates by chemical means and under conditions such that the liberation of the ClO_3' ion cannot be assumed.

We have evidence that this is true in the fact that chlorates when heated to moderate temperatures produce perchlorate, one portion of the chlorate furnishing oxygen for the oxidation of another portion; a reaction which may be represented by:

$$4NaClO_3 = NaCl + 3NaClO_4$$

The possibility of a direct oxidation was even more

strikingly shown by Fowler and Grant.[1] They found on heating chlorate with silver oxide that the chlorate was completely converted to perchlorate without the loss of oxygen, metallic silver being the other product.

It was desired, however, to show that the oxidation could be brought about in an aqueous solution and for this purpose several oxidizing agents were selected as the most useful and their action on sodium chlorate investigated as described below.

Method of Analysis

The method used for determining the amount of the various chlorine acids in the presence of each other was essentially that described by Treadwell-Hall[2] and is briefly as follows: In a solution containing chlorides, chlorates and perchlorates, or the corresponding free acids, the amount of chlorine as chloride was determined directly by titration of one sample (1). A separate portion (2) titrated, after reduction with ferrous sulphate with an excess of dilute sulphuric acid, gave the amount of chlorine as chlorate plus that as chloride. A third portion (3) of the solution after evaporation to dryness with sodium carbonate was fused in a tall platinum crucible, the mouth being closed by a plug of loosely packed asbestos fiber. This sample showed the total amount of chlorine present in all forms. The amount of chloride present in the original solution is, then, shown by (1), that as chlorate by the difference between that found in (2) and (1), and that present as perchlorate by the difference between the amount shown by (3) and (2).

The amount of chlorine in these samples was in all cases determined[3] by addition of an excess of tenth normal silver nitrate solution, filtering off the precipitated silver chloride and titrating the excess silver nitrate with a tenth normal solution of ammonium sulphocyanate, using ammonium ferric

[1] Jour. Chem. Soc., **57**, 272 (1890).

[2] Analytical Chemistry, p. 463 (1911).

[3] Sutton: Volumetric Analysis, 9th Ed., p. 172.

alum as indicator. This method was found to be rapid and gave consistent and very accurate results. Duplicate samples containing 0.3 gram chlorine frequently gave results differing by only 0.3 milligram.

In addition to the quantitative determination all solutions were examined for the presence of perchlorates by the microchemical test described by van Breukeleveen.[1]

Experiments with Persulphate

The first oxidizing agent studied was sodium persulphate. This is commonly considered as a very powerful oxidizing agent and it seemed probable that it might convert chlorate to perchlorate even in aqueous solution. This was established as true by the following experiments.

Preliminary Experiment.—A solution containing about 5 percent of sodium chlorate was boiled for 10 minutes with an excess of sodium persulphate. After evaporation to dryness concentrated hydrochloric acid was added and the solution again evaporated, on a water bath, to convert all remaining chlorate to chloride. After dissolving the residue in water, silver nitrate was added until all chloride present was removed. After filtering the solution was evaporated, the residue fused with sodium carbonate, dissolved in dilute nitric acid and silver nitrate added. A heavy precipitate of silver chloride indicated that a portion of the chlorate originally present had been converted to perchlorate.

Experiments 8–12.—One gram portions of sodium chlorate, representing 0.3324 gram chlorine as chlorate, were boiled with solutions of sodium persulphate, the conditions being as shown below. In all cases a considerable oxidation to perchlorate was found. Tests of the several solutions for chlorides, after boiling with persulphate, showed the absence of chlorine in this form. We have to deal with chlorine as chlorate and perchlorate only. The latter was determined by difference in the first experiments.

[1] Rec. Trav. chim. Pay-Bas., **17**, 94 (1898).

	8	9	10	11	12
Chlorine (as chlorate) taken	0.3324	0.3324	0.3324	0.3324	0.3324
Water, cc.	100	100	100	25	25
Sodium persulphate (grams)	10	10	10	10	10
Length of time heated (minutes)	30	30	60	30	30
Chlorine (as chlorate) found	0.2710	0.2705	0.2736	0.2730	0.2751
Percentage oxidized to perchlorate	18.47	18.32	17.69	17.87	17.24

While these experiments showed in a satisfactory manner that chlorate may be oxidized to perchlorate by means of persulphate, it was desired, if possible, to establish conditions under which the oxidation would take place more efficiently, since it was noted that a large amount of oxygen was evolved during the reaction in the previous experiments. It has been pointed out[1] that the presence of silver salts seems to affect favorably the oxidizing power of persulphates, many substances being easily oxidized in this manner which are scarcely affected by persulphate alone.

Experiment 26.—One cc of tenth normal silver nitrate was added to a solution containing one gram sodium chlorate in 25 cc (representing 0.3324 g Cl) and 10 g sodium persulphate. Boiled one-half hour.

<div align="center">ANALYSIS</div>

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.2565 gram
Oxidized to perchlorate	0.0759 gram
Oxidized to perchlorate	22.83 percent

This experiment confirmed the fact that the presence of even small amounts of silver salts increased the oxidizing power of persulphates. Since this phenomenon has been ascribed to the fact that silver salts catalytically increase the velocity

Price. Per-Acids and Their Salts, p. 35 (1912).

with which persulphate decomposes, and since this decomposition may be represented by

$$Na_2S_2O_8 + H_2O = 2NaHSO_4 + O,$$
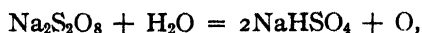
it seemed probable that under conditions such that the sulphate ion would be removed from the sphere of reaction as fast as formed, the velocity of decomposition and the oxidizing power might be favorably affected. This was confirmed as follows:

Experiment 31.—A solution, containing in 100 cc, one gram sodium chlorate, 10 grams sodium persulphate and 13 grams barium oxide, was boiled for 30 minutes. After removal of the barium sulphate, an analysis gave the following results:

ANALYSIS

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.2202 gram
Oxidized to perchlorate	0.1122 gram
Oxidized to perchlorate	33.75 percent

Although it seemed certain that in the previous experiments the oxidation was due solely to the persulphate present, the statement is frequently made that dilute solutions of chloric acid or weakly acid solutions of chlorates are somewhat oxidized to perchlorate on boiling. To determine whether this was true for the conditions employed in the experiments described two solutions were made up containing in 25 and 100 cc, respectively, an amount of sulphuric acid and of sodium sulphate corresponding approximately to the end products of decomposition of 10 grams sodium persulphate; that is, 6 grams sodium sulphate and 2.1 cc sulphuric acid (sp. gr. 1.82). To each of these one gram sodium chlorate was added and the solution boiled for 15 minutes. Neither the usual analysis nor the microchemical test showed the presence of perchlorate in either solution after this treatment. This shows conclusively that the oxidation obtained in experiments previously described is to be assigned to the sodium persulphate.

In all cases described the microchemical test[1] showed the

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[1] Van Breukeleveen, loc. cit.

presence of considerable quantities of perchlorate. It seemed
desirable, however, to determine analytically the quantity
of perchlorate present. This was done as follows:

Experiment 40.—One gram sodium chlorate, containing
0.3305 gram Cl as chlorate, added to 10 grams sodium per-
sulphate in 25 cc water. Boiled 30 minutes.

<div align="center">ANALYSIS</div>

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.2886 gram
Total chlorine found after treatment	0.3312 gram
Oxidized to perchlorate	0 0626 gram
Oxidized to perchlorate	18 94 percent

These experiments establish satisfactorily that chlorate
can be oxidized to perchlorate by means of sodium persulphate.

Experiments with Ozone

Although the action of ozonized oxygen on solutions of
chlorates was investigated by Oechsli[1] the result of his ex-
periments is hardly conclusive, since one case in which a 2.5
percent sodium chlorate solution was saturated with ozonized
oxygen for 8 hours, showed a decrease of 1.2 percent in the
chlorate content. A following experiment, in which free
chloric acid was substituted for the sodium chlorate, gave a
decrease of 0.34 per cent in chlorate as a result of the treat-
ment with ozone. The conclusion reached, however, was
"das eine Oxydation des ClO_3 Ions durch ein etwa 6 Volum-
prozent Ozon enthaltendes Gas nicht bewirkt werden kann."

It seemed desirable, therefore, to carry on experiments
with ozone in order to determine whether a larger proportion
of the chlorate might not be oxidized by this means.

Experiment 25.—Ozonized oxygen for this experiment
was generated by passing dry oxygen through a Siemens
ozonizer, the high tension current being supplied by a 10,000
volt transformer of 1 KVA capacity. The gas thus generated
was bubbled through the chlorate solution contained in a

[1] Zeit. Elektrochemie, **9**, 821 (1903).

large test-tube, the length of the experiment being 19 hours and the temperature of the solution 22 °. The solution contained 1 gram sodium chlorate and 1 cc sulphuric acid (sp. gr. 1.82) in 25 cc.

ANALYSIS

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.3298 gram
Oxidized to perchlorate	0.0026 gram
Oxidized to perchlorate	0.78 per cent

Since it is known that silver oxide decomposes ozone catalytically, it was thought that the presence of this substance might have a favorable effect on the oxidizing power. This seemed especially probable in view of the increased oxidation obtained with persulphate through the presence of silver salt.

Experiment 28.—Solution consisted of one gram sodium chlorate, 1 cc of normal nitric acid, 0.10 gram silver oxide and 25 cc water. Ozonized oxygen was bubbled through the solution for 20 hours, the temperature of solution being 22° C. Results of analysis follow:

ANALYSIS

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.3262 gram
Oxidized to perchlorate	0.0062 gram
Oxidized to perchlorate	1.86 percent

Experiment 32.—The solution used was the same as in the previous experiment but was maintained at 100° C. Ozonized oxygen was passed through the solution for 5 hours. Result of analysis follows:

ANALYSIS

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.3301 gram
Oxidized to perchlorate	0.0023 gram
Oxidized to perchlorate	0.69 percent

Although no attempt was made in the previous experiments to regulate the ozone concentration of the ozonized oxygen used, it was known to be about 7 percent by volume.

It seemed probable that a gas with higher ozone concentration might be more effective in obtaining the desired oxidation. An apparatus was, therefore, constructed which was capable of producing oxygen containing a very high percentage of ozone. The ozone was produced by electrolysis of sulphuric acid solutions at low temperatures. The apparatus employed was essentially a modification of that described by Fischer and Massenay.[1]

No attempt was made to control the concentration of ozone produced by this apparatus but it continuously furnished a gas of very much higher ozone content than that from the Siemens tube. One analysis showed a concentration of 21 percent ozone by volume.

Experiments 38 and 39. Solutions containing one gram sodium chlorate and 2 cc sulphuric acid (sp. gr. 1.82) in 25 cc water were used and were maintained at 100° by means of a water bath. Ozonized oxygen produced by the apparatus described was allowed to bubble through these solutions for two hours. As in the previous cases a slight oxidation of the chlorate was obtained.

<div align="center">ANALYSIS</div>

	38	39
Chlorine (as chlorate) taken	0.3324 gm	0.3324 gm
Chlorine (as chlorate) found after treatment	0.3300 gm	0.3296 gm
Oxidized to perchlorate	0.0024 gm	0.0028 gm
Oxidized to perchlorate	0.71%	0.82%

The experiments with ozone show, therefore, that while ozone is capable of oxidizing acid solutions of chlorates, the oxidation is not at all efficient. In all cases described the amount of ozone used was in excess of the theoretical amount necessary to oxidize all chlorate present. It may be pointed out that while the amount oxidized is small it is nevertheless certain that perchlorate was produced since the

microchemical test showed, unquestionably, the presence of perchlorate in all solutions after treatment with ozone.

Since acid solutions of permanganates are known to be strong oxidizing agents, this was the next material studied.

Experiment 45.—A solution containing one gram sodium chlorate, 1 cc sulphuric acid (sp. gr. 1.82) and one gram potassium permanganate in 100 cc water was boiled for 30 minutes. The solution showed no perchlorate present.

ANALYSIS

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.3326 gram

This experiment shows that acid solutions of potassium permanganate will not oxidize chlorate to perchlorate.

The next oxidizing agent studied was aqueous sodium peroxide.

Experiment 46.—A solution containing one gram sodium chlorate and 10 grams sodium peroxide in 25 cc was boiled for 15 minutes. After cooling and diluting to 100 cc the solution was acidified with dilute nitric acid.

ANALYSIS

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.3317 gram

The slight discrepancy noted here between the amount of chlorate taken and that found after treatment is probably to be regarded as experimental error since the microchemical test used failed to show the presence of perchlorate. The amount represented by the difference in the two chlorine determinations is probably within the experimental error in this case since the presence of large amounts of sodium salts in the solution made the analysis somewhat less accurate than in previous cases.

Experiments with Hydrogen Peroxide

Hydrogen peroxide is probably to be considered as one of the strongest of oxidizing agents since its decomposition

must be accompanied by the generation of atomic or active oxygen:

$$H_2O_2 \longrightarrow H_2O + O_1$$

Although not commonly so considered it should be a stronger oxidizing agent than ozone since the decomposition of the latter is represented by

$$O_3 \longrightarrow O_2 + O_1.$$
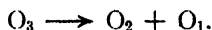
The concentration of active oxygen in the case of the hydrogen peroxide is thus seen to be much higher. Consequently its oxidizing power must be correspondingly greater.

The action of hydrogen peroxide on chlorate solutions was, therefore, next investigated.

Alkaline solutions of hydrogen peroxide were used as oxidizing agents. A solution containing one gram sodium chlorate and 1 cc ammonium hydroxide (sp. gr. 0.90) in 15 cc perhydrol was boiled for 30 minutes. Analysis of the solution gave the following results:

ANALYSIS

Chlorine (as chlorate) taken	0.3305 gram
Chlorine (as chlorate) found after treatment	0.3298 gram

No perchlorate could be found in the solution by microscopic test. The experiment, therefore, shows that alkaline hydrogen peroxide is not a sufficiently powerful oxidizing agent to convert chlorates to perchlorates.

Experiment 47. One gram of sodium chlorate was dissolved in 15 cc perhydrol (Merck's 30 percent) and the solution evaporated to dryness on the water bath. The residue was dissolved in a second 15 cc portion of perhydrol and again brought to dryness. After dissolving the residue in water the following analysis was obtained:

ANALYSIS

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chlorate) found after treatment	0.3327 gram

This experiment shows that chlorate in neutral solutions is not oxidized to perchlorate by 30 percent hydrogen peroxide.

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It is undoubtedly true that oxidizing agents, in general, are more powerful in the presence of acid than in neutral or alkaline solutions. Therefore, it was decided to investigate the action of hydrogen peroxide on acid solutions of chlorates. Some work has been done along this line by Tanatar[1] who investigated the action of hydrogen peroxide on halogen oxyacids. He found that hydrogen peroxide had no effect on either neutral or acid solutions of chlorates, while bromates were quickly reduced to bromide with evolution of some bromine. These conclusions are certainly in error in so far as they state that acid chlorate solutions are unaffected by hydrogen peroxide. This will be seen from the following experiments.

Experiment 48.—One gram sodium chlorate was dissolved in 25 cc of 30 percent hydrogen peroxide which had previously been acidified by 1 cc sulphuric acid (sp. gr. 1.82). The solution was boiled for one hour. Soon after the solution had reached the boiling point a yellow gas was evolved. This was at first thought to be chlorine but more careful examination showed it to be a mixture of chlorine dioxide and chlorine. The microchemical test showed the presence of perchlorate in the solution and analysis gave the following results:

ANALYSIS

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as choride) found after treatment	0.2916 gram
Chlorine (as chlorate) found after treatment	0.0030 gram
Total chlorine found after treatment	0.2927 gram

This experiment shows that chlorate, through the action of acid solutions of hydrogen peroxide, is largely converted to chloride. A considerable amount of chlorine and chlorine dioxide is evolved at the same time.

Experiment 49.—The conditions in this experiment were the same as in the previous case with the exception that 3 percent hydrogen peroxide was used. The solution was boiled for 12 hours.

[1] Ber. deutsch. chem. Ges., **32**, 1013 (1899).

Chlorine (as chlorate) taken	0.3324 gram
Chlorine (as chloride) found after treatment	0.0122 gram
Chlorine as chlorate, found after treatment	0.3162 gram

This experiment, again, shows that by the action of acid hydrogen peroxide solutions on chloride we have an apparent reduction to chloride. This was confirmed by a series of experiments which all gave results similar to those described above.

It now became necessary to account for the *apparent* reducing action which hydrogen peroxide exerted on acid chlorate solutions. The fact that chlorine and chlorine dioxide were set free during this reaction caused no difficulty. The presence of a small amount of hydrochloric acid in the solution would be sufficient to account for this, since it is known that hydrochloric acid solutions rapidly decompose chlorate, particularly when heated to 80°. This decomposition may be represented by

$$HClO_3 + HCl \longrightarrow H_2O + ClO_2 + Cl.$$

It seemed certain, therefore, that the main reaction with which we were dealing, was an apparent reduction of chloric to hydrochloric acid, and that the evolution of chlorine and chlorine dioxide was to be considered as a secondary reaction due to the action of hydrochloric acid on chlorate, which still remained undecomposed.

To account for the apparent reducing action shown here by hydrogen peroxide several possibilities presented themselves. It seemed improbable that so strong an oxidizing agent as hydrogen peroxide was here acting as a reducing agent, especially in view of the fact that many, if not all, of the apparent reductions, accomplished by hydrogen peroxide are in reality the result of oxidations to higher instable oxides[1] which immediately decompose if the experiment is conducted under ordinary conditions. Applying this idea to the case in question it was considered possible that the chloric acid was oxidized by hydrogen peroxide to a higher form,

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[1] This will be discussed more fully in a later paper.

which was unstable under ordinary conditions. Since the acid next higher than chloric acid is perchloric acid and this was shown to be perfectly stable under the conditions existing in the experiments it was necessary to assume the formation of an acid still higher than perchloric. The further assumption necessary was that this hypothetical higher acid would decompose spontaneously with the liberation of oxygen and formation of hydrochloric acid.

Assuming for the moment the existence of this compound it seemed highly probable that during its formation from chloric acid we would pass through the perchlorate stage or, in other words, that it should be formed equally well from perchloric acid.

A preliminary experiment showed, however, that this theory was untenable. A 5 percent solution of potassium perchlorate acidified with sulphuric acid was added to an equal volume of 30 percent hydrogen peroxide and the whole boiled for 10 minutes. No chlorides were present in the solution after this treatment. This experiment is supported by the work of Tanatar[1] who found that perchloric acid is not affected by hydrogen peroxide. It became necessary, therefore, to abandon the position first taken.

The possibility next considered was the existence of a molecular compound between chloric acid and hydrogen peroxide. No assumptions were made as to the nature of this hypothetical compound but for the time being it was considered analogous to the possible compounds between ferrous sulphate and hydrogen peroxide described by Mummery.[2] The hypothesis which we are now considering postulated, of course, that this compound $HClO_3.xH_2O_2$, if existent, would decompose with formation of hydrochloric acid.

If this compound were actually formed on mixing solutions of chloric acid and hydrogen peroxide it seemed probable that its presence would be revealed by a measurable thermal change. Accordingly the heat of dilution of solutions of

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[1] Ber. deutsch. chem. Ges., **32**, 1013 (1899).

[2] Jour. Soc. Chem. Ind., **32**, 889 (1913).

chloric acid with hydrogen peroxide was determined as follows:

Experiment 50.—The apparatus used consisted of a silvered Dewar flask of about 200 cc capacity, fitted with a stopper carrying a small funnel tube and a 100° thermometer, graduated in 0.1°. The stopper was also cut away at one side to permit the introduction of a glass stirring rod.

Twenty cc of a 5 percent chloric acid solution was introduced into the flask and the temperature allowed to become constant. 5 cc 30 percent hydrogen peroxide solution were then brought to the same temperature and introduced into the flask. The temperature of the mixture rose rapidly and reached a value where it remained constant for several minutes. The thermal effect on diluting 20 cc of 5 percent chloric acid with 5 cc of water was next determined, the procedure being exactly similar to that used in the previous case. The data obtained were as follows:

Initial temperature of chloric acid	24.70°
Initial temperature of hydrogen peroxide	24.70°
Maximum temperature of mixture	24.95°
Rise in temperature of mixture	0.25°
Initial temperature of chloric acid	24.55°
Initial temperature of water	24.55°
Maximum temperature of mixture	24.80°
Rise in temperature of mixture	0.25°

These experiments are sufficient to indicate that there is little possibility of the formation, at room temperature, of a compound between chloric acid and hydrogen peroxide. One possibility remained to be considered, however, before abandoning this hypothesis. It has been mentioned that the apparent reducing action of hydrogen peroxide on chloric acid does not become evident until a temperature of about 80° is reached. The possibility existed, therefore, that the intermediate compound just considered might be formed at a point somewhat above room temperature. If this were true the formation of the compound would be indicated by a break in the heating curve of a mixture of chloric acid and hydrogen peroxide. An investigation of the heating curve of a 5 percent chloric acid solution mixed with an equal volume

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of 30 percent hydrogen peroxide failed to show any break which would indicate the formation of a compound.

The conclusion was, therefore, reached that the *apparent* reduction of chlorate to chloride by hydrogen peroxide could not be assigned to the formation of an instable compound between the two.

The most satisfactory explanation of this phenomenon, however, was found in the fact that in a dilute solution of chloric acid we have a small amount of chlorine liberated through spontaneous decomposition of the acid. This chlorine, by its action on the hydrogen peroxide, immediately forms hydrochloric acid.[1] The hydrochloric acid thus produced would, of course, immediately attack the remaining chlorate, the products of this reaction being hydrochloric acid, chlorine, chlorine dioxide and oxygen. The reaction is, therefore, auto-catalytic, and a small amount of hydrochloric acid is sufficient to start the decomposition. It has been mentioned that the formation of chlorides in a solution of chloric acid and hydrogen peroxide, does not begin to be appreciable until the temperature is raised to about 80°. This is in accord with the work of Sand[2] who investigated the reaction between chloric acid and hydrochloric acid. He found that the velocity of the reaction became appreciable at temperatures above 70°.

This explanation of the apparent reducing action of hydrogen peroxide on chloric acid has the advantage that it makes no assumptions whatever but uses only well-known facts to account for the phenomenon. There is scarcely room for doubt that the explanation put forward represents the true mechanism of the reaction. It also shows that hydrogen peroxide does not here act as a reducing agent, in the true sense of the term.

Experiments with Activated Oxygen

The fact that oxygen is activated or ionized by ultra-

[1] Fairley: Jour. Chem. Soc., **31**, 22 (1877).

[2] Zeit. phys. Chem., **50**, 465 (1904).

violet light rays is well established.[1] In this condition it is a very powerful oxidizing agent, probably stronger than either ozone or hydrogen peroxide. The action of activated oxygen on chloric acid was, therefore, investigated.

It is frequently stated that solutions of chloric acid are slowly oxidized on standing in sunlight. While this is probably true, the necessity for the presence of oxygen has not been recognized.

A solution was made up containing 0.4784 gram sodium chlorate and 0.25 cc sulphuric acid (sp. gr. 1.820) in 45 cc. This represented 0.1582 gram chlorine as chlorate. The solution was placed in a transparent quartz flask and a neutral atmosphere maintained by continuously passing in nitrogen which had been freed from traces of oxygen by washing with alkaline pyrogallol solution. Ultraviolet light was obtained by means of a Cooper Hewitt quartz tube mercury arc lamp, the flask containing the solution being suspended about 5 cm from the lamp. The experiment continued for 28 hours. No oxidation of the chlorate took place, as is shown by the analysis.

<center>ANALYSIS</center>

Chlorine (as chlorate) taken	0.1582 gram
Chlorine (as chlorate) found after experiment	0.1580 gram

This experiment shows conclusively that, in the absence of oxygen, dilute chloric acid solutions are not photochemically oxidized to any appreciable extent.

The next experiment was similar to the preceding one, except that oxygen was continuously bubbled through the solution. The flask held 50 cc of solution containing 1.000 gram of sodium chlorate and 0.50 cc sulphuric acid (sp. gr. 1.820). This represents 0.3305 gram chlorine as chlorate. The solution was subjected to the action of the ultraviolet rays for 8 hours. After the treatment, the microchemical test showed perchlorate to be present. This was confirmed by analysis.

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[1] Sheppard: Photo-chemistry, p. 253 (1914).

ANALYSIS

Chlorine (as chlorate) taken	0.3305 gram
Chlorine (as chlorate) found after experiment	0.3269 gram
Oxidized to perchlorate	0.0036 gram
Oxidized to perchlorate	1.09 percent

It was desired to determine whether more of the chlorate could be oxidized by longer treatment with the activated oxygen.

Accordingly, a solution of sodium chlorate was made up and found, by analysis, to contain 0.1172 gram in 10 cc. The solution was acidified slightly (0.5 percent) with sulphuric acid. The other conditions being as in previous experiments the solution was subjected to the ultraviolet rays, oxygen being continuously bubbled through. 10 cc samples, for analysis, were withdrawn at regular intervals. The results follow:

Time elapsed (hours)	Sodium chlorate found per 10 cc solution
0	0.0072
24	0.1158
72	0.1160
96	0.1157

It will be noted that during the first 24 hours a small amount of the chlorate was oxidized. This represents about 1.1 percent of the total amount present. During the remaining time no further oxidation took place. It will also be noted that these results are practically identical with those obtained when ozonized oxygen was used as the oxidizing agent, as well as with those obtained by Oechsli[1] with ozone. It has proved impossible to account satisfactorily for the fact that the oxidation of the chlorate stops when approximately one percent has been converted to perchlorate. The possibility of perchloric acid being instable under ultraviolet rays was considered and investigated. If this were true, after exposing

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[1] Zeit. Elektrochemie, **9**, 807 (1903).

the acid to ultraviolet light we should expect to find some of the chlorine present as one of the lower oxy-acids, presumably as chlorate. A solution containing about 2 percent perchloric acid was placed in a quartz test-tube and oxygen slowly bubbled through the liquid. The tube was exposed to the rays from the mercury arc lamp for several hours. Examination of the solution showed that all of the chlorine remained in the form of perchlorate. The hypothesis mentioned is, therefore, untenable.

The possibility remains that active oxygen is less stable in the presence of perchloric acid than under ordinary conditions. This is equivalent to saying that perchloric acid catalyzes the reaction $2O_1 = O_2$ and hence tends to keep the concentration of active oxygen down. We know that under the conditions maintained the concentration of this substance is very low, at best, and the presence or formation in the solution of any substance which tended to convert it to the molecular form might force its concentration below the point necessary for chlorate oxidation. There seems to be no satisfactory way of testing this hypothesis, however, and it must stand simply as a suggestion which, if true, might account satisfactorily for the facts observed. This phase of the problem should be further investigated with a view to determining what stops the formation of perchlorate when a certain amount has been produced and whether the position of the equilibrium can be shifted by varying the concentration of active oxygen used. It seems probable that if the amount of active oxygen present or rather the rate of its production could be increased a further oxidation of chlorate would result.

In the experiments described in this paper, with the exception of those in which persulphate was used, the concentration of active oxygen attainable was necessarily low and not comparable, in degree, to that present at the anode during electrolysis. However, it is held that the conditions maintained duplicate *qualitatively* those at the anode during chlorate electrolysis and show that perchlorate can be formed by the direct addition of oxygen to the chlorate ion.

From what has been said above it may be concluded that:

1. Chlorate may be oxidized to perchlorate by persulphuric acid, ozone, and hydrogen peroxide in acid solutions.

2. In the case of hydrogen peroxide the hydrochloric acid formed interferes with the reaction.

3. This oxidation may also be carried on with oxygen activated by ultraviolet light.

4. The reaction is considered to take place according to:

$$HClO_3 + O_1 = HClO_4,$$
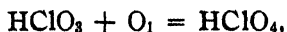
the quantity of oxidation depending on the concentration of active oxygen present.

5. Since active oxygen chemically produced oxidizes chloric acid to perchloric acid and since active oxygen is formed at the anode it follows that the electrochemical formation of perchlorate is the result of direct oxidation.

6. Perchlorate is formed at the anode at a potential far below that necessary for the continuous discharge of any ion present in the solution.

7. The conditions realized in the experiments described above duplicate, qualitatively, those existing at the anode during electrolysis.

Cornell University

NEW BOOKS

A Text-Book of Physics. *Edited by A. Wilmer Duff. Fourth edition revised. 21 × 15 cm; pp. xiv + 692. Philadelphia: P. Blakiston's Son and Co., 1916. Price: $2 75.*—The sections on Mechanics and Sound are written by A. Wilmer Duff, those on Wave Motion and on Light by E. Percival Lewis, and those on Conduction of Electricity through Gases and on Radioactivity by R. K. McClung; while Charles E. Mendenhall writes about Heat, and Albert P. Carman about Electricity and Magnetism.

The reviewer was delighted to read the paragraph on p. 643 "Nebulae give bright line spectra, some of the lines being due to hydrogen and helium, while others have not yet been identified. The spectrum of comets consists mostly of the characteristic hydrocarbon bands similar to those given by the green cone of the Bunsen flame. It seems evident in the cases of nebulae and comets that the radiation is an example of luminescence, or luminosity due to other causes than high temperature, because these bodies appear to consist of masses of highly attenuated gases, or small bodies, and it is inconceivable that their temperature can remain permanently much higher than that of the surrounding space."

There is another paragraph of distinct interest to chemists on p. 601. "It seems quite possible that the change of index of refraction at the boundary [between two phases] is not abrupt, but that there is a transition layer due to the interpenetration of the two media, or occlusion at the surface, causing a gradual change in the index. If this be the case, total reflection may be considered as altogether due to refraction. When the angle of incidence is equal to or greater than k [the critical angle] the wave front in the transition layer will swing around and become normal to the surface; then the lower edge will gain on the upper and the wave will swing back into the first medium. If we consider an air film between two refracting media the two transition layers may encroach on each other, in which case the lower edge of the wave will be retarded, and a part of it will pass into the third medium It might be expected, therefore, that if the air film from which total reflection takes place is very thin, total reflection will cease. This has been found to be the case. If a right-angled total reflecting prism with a slightly convex hypothenuse surface is pressed against a glass plate, total reflection takes place from the hypothenuse of the prism when the angle of incidence is sufficiently large, but some light will always be transmitted through the region surrounding the point of contact even where the air film has a measurable thickness. It is found that the thickness of the air film through which transmission can occur (which may be considered as approximately the thickness of the transition layer) differs with the wave-length and with the angle of incidence, and may reach several thousandths of a millimeter."

On p. 525 under Sound, we read that "diffraction means the bending of waves around obstacles. It prevents the formation of sharp shadows. The amount of diffraction in any case depends on the linear dimensions of the obstacle compared with the wave-length of the sound. A hill casts a fairly definite sound shadow because it is large in comparison with the wave-length. Cases have been known in which houses in the shadow of a hill suffered no damage from very loud

sounds, such as the explosion of a powder magazine or the firing of cannon, while the windows of equally distant houses not in the shadow were broken by the impact of the sound waves. But small obstacles, such as trees and posts, cast no observable sound shadows, except when tested by waves of very short length. The human head is of sufficient size to cast something of a shadow for sounds of high pitch. If the sound is to the left or the right of the observer, one ear is in this partial shadow and from the relative intensities as heard by the two ears we judge of the direction of the source. Long waves produce about equal intensities at the two ears, but at one ear the phase of the waves is later than at the other and it has been shown that it is by this slight difference that the mind unconsciously judges of the direction of the source of the sound."

It would have been interesting if the author had pointed out why it is as difficult as it is said to be to tell the direction from which a lion's roar comes.

On p. 162 is given an account of Langmuir's new mercury vapor pump, which is apparently the most efficient and most rapid pump in existence. Langmuir's pump will exhaust a vessel of 11 liters' capacity from atmospheric pressure to a vacuum of 0.00001 mm in 80 seconds.

The remarks on miscellaneous properties of solids, p. 119, are worth quoting. "There are many mechanical properties of solids, frequently mentioned, which are not yet defined with sufficient clearness to make it possible to measure them, but which call for some mention. A *malleable* body is one which can be hammered into thin sheets . . . . . A *ductile* substance is one which can be drawn out into fine wires. . . . . .

"A *plastic* substance is one which can be moulded by pressure. Many substances not ordinarily regarded as plastic are so, when subjected to great pressure slowly applied. A stick of sealing-wax is ordinarily brittle, but, suspended horizontally on end supports, it will yield slowly to its weight and bend. All metals under enormous shearing stresses become plastic. The impact of a cannon ball on armor plate will sometimes produce a splash like a stone dropped in water.

"A *friable* substance is one easily reduced to powder by a blow. Glass, diamonds and crystals are friable.

"*Hardness* is a term used in different senses. It sometimes means the opposite of plasticity, that is, resistance to change of shape, as when we speak of iron as hard and rubber as soft. Another use of it is to denote power of scratching, as in the mineralogists' scale of hardness, which consists of a series of substances, beginning with diamond at one end and talc at the other, arranged so that each, beginning with diamond, will scratch the following but not the preceding. Any other substance that will scratch one in the list but not the next higher is said to have a hardness between the two."

On p. 157 we find that "when a gas is in contact with a solid there are molecular forces drawing the particles together, and these produce more or less condensation of the gas on the surface of the solid. This makes it impossible to remove the last traces of a gas from a glass vessel by means of an air pump. It also accounts for the fact that, when a figure is traced on a sheet of glass by a stick, the figure will appear when the glass is breathed on. The breath condenses less readily on the part of the glass that has been freed from condensed gas by the scraping of the stick. [This implies that the gas film is taken up slowly. It

is not clear why moisture should condense on the air film rather than on the glass.]

"A porous solid is readily permeated by a gas and condensation on the surfaces of the pores takes place. This is called *occlusion*. Very porous wood charcoal will absorb nine volumes of oxygen, thirty-five volumes of carbonic acid, and ninety volumes of ammonia per volume of the charcoal, and cocoanut charcoal will absorb still more. This is why charcoal is so useful as a deodorizer. Platinum in the porous form called platinum sponge will absorb 250 times its own volume of oxygen. Palladium will absorb more than one thousand volumes of hydrogen. Its own volume is thereby increased by about one-tenth. The hydrogen is, therefore, reduced to one-thousandth [ten-thousandth?] of its original volume; to produce such a condensation by pressure alone would require a pressure of several tons per square inch." *Wilder D. Bancroft*

The Chemistry and Technology of Mixed Paints. *By Maximilian Toch. Second revised edition. 23 × 16 cm; pp 366. New York: D. Van Nostrand Company, 1916. Price: $4.00.*—The first edition of this admirable book appeared in 1907 and contained 160 pages. The extent of the revision may be guessed from the fact that the present volume has 353 pages. The subject is treated under the headings: the manufacture of mixed paints; the white pigments; the oxides of lead; the red pigments; the brown pigments; the yellow pigments; the blue pigments; the green pigments; the black pigments; the inert fillers and extenders; mixed paints; linseed oil; Chinese wood oil; soya bean oil; fish oil; miscellaneous oils; turpentine; pine oil; benzine; turpentine substitutes; cobalt driers; combining mediums and water; fine grinding; the influence of sunlight on paints and varnishes; paint vehicles as protective agents against corrosion; the electrolytic corrosion of structural steel; painters' hygiene; the growth of fungi on paint; analysis of paint materials.

In 1909 Soya bean oil was practically unknown as a paint oil whereas now we read, p. 201: "It is not within the province of the writer to forecast the future of any paint oil; but there is no doubt that if a campaign of education be waged among the farmers, particularly in those states where soil has been regarded as unproductive, and the properly selected seeds of soya beans are planted, no scarcity in the flax seed crop will ever again be a menace to the paint and varnish industries . and after the ground has been productive of soya beans for some time, it will be fit for the growing of even the most difficult of crops."

Pine oil is another new and useful material though by no means a substitute for linseed oil or turpentine, p. 234. It is a very powerful solvent, and many of the acid resins which have a tendency to separate when they are insufficiently heated with drying oils will remain together when pine oil is added. Pine oil can be used to a considerable extent as a diluent in nitrocellulose solutions; and as a cooling agent for the reduction of varnishes it also has excellent qualities.

As might be expected, the author is enthusiastic about China wood oil, p. 181. "It is pretty well agreed that at 450° F. China wood oil gelatinizes, and if allowed to cool becomes insoluble. But experts in the manipulation of China wood oil add metallic salts or resinates at this temperature and a small percentage of untreated linseed oil, and, before it is sufficiently cool, small quantities of naphtha and benzol. The resulting liquid is a clear varnish-like oil which

dries with a hard elastic film, much more slowly than the original China wood oil. In this condition it possesses most remarkable qualities. By the use of China wood oil paints are made which dry in damp atmospheres. The advantage which the Chinese and Japanese have over the Europeans on this subject has been recognized for a long time. It is now known to have been due to their knowledge of the proper manipulation of China wood oil. For the making of marine paints and waterproof paints China wood oil is indispensable."

The author believes that a dried film of linseed oil is not porous, excepting for the air bubbles which may be bedded in it, but that any dried film of linseed oil subjected to moisture forms with it a semi-solid solution, and the moisture is carried through the oil to the surface of the metal, p. 166. "If a drop of linseed oil is spread on a glass slide and one-half of it covered with a cover glass, it will readily be seen under the microscope that the dried film is as solid as the glass itself and that there are no pores nor any semblance to a reticulated structure visible in the oil and the author therefore makes the statement with absolute certainty that linseed oil dries with a homogeneous film in all respects similar to a sheet of gelatine or glue."

This conclusion may be right, but the evidence on which it rests is insufficient. Without having tried it, the reviewer is quite certain that it would be impossible to see any reticulated structure in one of Bechhold's ultra-filters and yet these must be porous.

The author points out clearly that white lead in oil tends to chalk while zinc oxide causes oil to dry very hard, p. 142, and consequently that a mixture of the two is better than either alone. What relative proportions should be taken depend on the local conditions of exposure and climate. Special stress is laid, pp. 16, 34, 110, 119, on the point that the use of inert fillers such as barium sulphate adds very much to the wearing properties of the paint, and consequently these substances should not be considered as adulterants. Of course the presence of these substances in the paint should not be concealed. Although the author calls attention to the presence of calcium sulphate, silica, etc., in Venetian red, ochres, and umbers, he does not point out clearly the conditions under which a natural or added filler has only a slight effect on the tint. That will come in the next edition   On the other hand, the author accepts O'Brien's theory in regard to the darkening of lithopone.

The reviewer was much interested in the pages on concrete paints, p. 147. "It is well known that concrete of any kind and of any mixture is rapidly disintegrated by paraffin or machinery oils and reduced in time. If, however, the cement filler or neutralizing liquid is composed of China wood oil and a hard resin like copal, the resulting calcium resinate becomes insoluble in oil, so that oil dripping on a floor of this kind does not disintegrate the Portland cement. Oil collecting on an unpainted concrete floor will cause the floor to become as soft as cheese in time, and then there is no remedy for it excepting to take up the floor and put down a new one."

The first edition was a good book and the second edition is incomparably better than the first.　　　　　　　　　　　　　　*Wilder D. Bancroft*

EQUILIBRIUM IN THE SYSTEM: MERCURIC IODIDE–PYRIDINE

BY J. HOWARD MATHEWS AND PHILIP A. RITTER

Pyridine has long been recognized as an unusual organic solvent, especially as regards its power of dissolving inorganic salts and forming compounds with them. While it is true that alcohol, acetone and other organic solvents often form compounds analogous to hydrated salts, pyridine does this to an unusual extent, the combination of salt and pyridine often occurring in several different ratios.

The object of the work to be here described, which is but a part of an extensive series of similar investigations[1] carried on in this laboratory, was to study the phase relations for mercuric iodide and pyridine. Monari,[2] in 1884, while working with mercuric iodide in pyridine solution observed the formation of large, colorless crystals which he found corresponded to the formula $HgI_2.2C_5H_5N$. Other investigators[3] since then have isolated the same compound, but beyond describing a few of its properties and confirming its formula as stated by Monari, no detailed study has been made and its solubility in pyridine has not been measured.

Merck's "Medicinal" pyridine was purified by the usual method used in this laboratory.[4] It was allowed to stand over caustic potash for a month, then over barium oxide and potassium permanganate for an equal period. It was then digested with barium oxide and permanganate under a reflux condenser for ten hours, and finally distilled, the fraction passing over between $114-116°$ being reserved for use. The mercuric iodide used was also a Merck preparation. It was recrystallized from pyridine, the crystals being drained and washed three times with pyridine, after which they were dried between

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[1] Jour. Phys. Chem., 12, 283 (1908); 13, 42 (1909); 14, 189 (1910); 16, 373 (1912); 18, 264 (1914); Jour. Am. Chem. Soc., 33, 1039 (1911).

[2] Jahresber., 1884, 629; Rev. chim. med. farm., 2, 190.

[3] Schroeder: Zeit. anorg. Chem., 44, 2 (1905); Groos: Archiv. Pharm., 228, 73 (1890).

[4] Wilcox: Jour. Phys. Chem., 14, 583 (1910).

sheets of clean filter paper. Gentle warming drives off the pyridine held in loose combination with the salt, leaving the latter in a pure condition.

For the temperatures —30° and above, mercury thermometers graduated to tenths and capable of being read to hundredths of a degree were used. All the temperatures above 0° were read from a Goetze thermometer which had been carefully compared with a similar thermometer standardized by the U. S. Bureau of Standards. From 0° to —30° the temperatures were read from a thermometer the corrections for which had been furnished by the U. S. B. S. From —30° to —50°, the temperatures were read from a toluene thermometer which had been compared at the points 0° and —30° with a thermometer standardized by the U. S. B. S.

The well-known solubility apparatus of Meyerhoffer and Saunders[1] was employed. It was fitted with a spiral glass stirrer and a mercury seal which effectually prevented loss of pyridine by evaporation, and ingress of water from the surrounding atmosphere. The solubility apparatus was immersed in a suitable gas-heated thermostat whose temperature was controlled by an ordinary toluene gas-regulator. For the temperatures above 60° a thin layer of paraffine aided materially in controlling the temperature by the prevention of evaporation. Temperatures between 20° and 0° were obtained by circulating a current of ice-water through a lead coil immersed in the same thermostat. For temperatures of 0° and below, the thermostat was replaced by a large, silvered Dewar cylinder. The point 0° was obtained by using finely crushed pure ice. The desired points below 0° were obtained by the use of freezing mixtures whose cryohydric points were suitable; the mixtures used being sodium thiosulphate and ice (—11°), sodium chloride and ice (—21.2°), and calcium chloride and ice (—55°). While the true cryohydric points were not reached, the temperatures which were obtained were constant, and served the purpose wholly satisfactorily. For points below —32°, solid carbon dioxide was used. In all cases the temperature was brought to the desired

[1] Zeit. phys. Chem., **28**, 464 (1899).

point and was kept constant for a period of three hours before samples were removed for analysis, the maximum variation in temperature during that time being $\pm0.1°$, and for the half hour immediately preceding sampling $\pm0.05°$, with the exception of the points $-40°$ and $-50°$, where the maximum variation was $\pm0.5°$. As our thermometer was not standardized for these lower temperatures and on account of the difficulty in keeping the temperatures sufficiently constant, not so much reliance is to be placed in the values obtained for the solubility of the salt in this region. However the error is not likely to be very large.

The samples for analysis were taken by the sampling device designed by Walton and Judd,[1] which insures no change in concentration during the process of sampling. Duplicate samples were taken at intervals of half an hour, to insure complete saturation, and in no case were data accepted where analysis of these duplicate samples did not agree.

Some difficulty in perfecting a quantitative method for the analysis of the samples was first encountered, due to the interference of the pyridine, but the one finally adopted proved wholly satisfactory. The sample of the mercuric iodide solution was dissolved in an excess of potassium iodide, and the whole diluted to 250 cc with distilled water. Hydrogen sulphide was then bubbled slowly through the cold solution until the mercury was completely precipitated. The precipitate was allowed to stand until the supernatant liquid became clear (which required about an hour), after which it was filtered through a Gooch filter. The precipitate was washed three times by decantation with hot water, then transferred to the Gooch crucible and washed three times with purified alcohol, after which it was dried at $115°$ for one hour. This method of analysis was tested on solutions of known concentrations of mercuric iodide in pyridine and was found to give thoroughly satisfactory results. The data obtained for the solubility of mercuric iodide in pyridine at different temperatures appear in the table below, and are shown graphically by the accompanying solubility curve.

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[1] Jour. Am. Chem. Soc., **33**, 1039 (1911).

Temperature	Wt. of sample	Wt. of HgS	Percentage of HgI_2
—50.0°	5.4666	0.0546	1.95
—50.0	5.6768	0.0554	1.91
—42.0	4.1520	0.0593	2.79
—42.0	4.7514	0.0674	2.77
—31.5	3.2840	0.0748	4.45
—31.5	2.3348	0.0488	4.09
—20.0	2.1992	0.0804	7.14
—20.0	3.0050	0.1152	7.49
—10.0	2.5624	0.1354	10.32
—10.0	2.1422	0.1124	10.25
— 0.1	2.3502	0.1750	14.86
— 0.1	2.5554	0.1944	14.85
+ 8.83	2.5564	0.2409	18.41
+ 8.83	2.6634	0.2513	18.43
20.02	1.4418	0.1800	24.38
20.02	1.2700	0.1588	24.42
25.55	0.8412	0.1205	27.97
25.55	0.7858	0.1120	27 84
35.28	2.2714	0.4032	34.67
35.28	1.7522	0.3090	34.45
40.08	1.8338	0.3538	37.68
40.08	1.9564	0.3766	37.60
42.58	2.2426	0.4516	39.33
42.58	2.1724	0.4344	39.06
45.10	2.3018	0.4832	41.01
45.10	1.9242	0.4038	40.99
47.72	2.4642	0.5344	42.36
47.72	2.1004	0.4548	42.32
50.02	1.9198	0.4242	43.17
50.02	1.5286	0.3375	43.13
55.05	1.1066	0.2574	45.44
55.05	1.1806	0.2767	45.57
57.07	1.3252	0.3182	46.90
57.07	2.1038	0.5064	47.02
60.07	1.2358	0.3060	48.36
60.07	0.7016	0.1732	48.22
70.35	2.1276	0.5761	52.88
70.35	2.9600	0.7990	52.73
80.05	3.0460	0.9008	57.76
80.05	2.2172	0.6520	57.44
90.08	2.5288	0 7962	61.50
90.08	3.4620	1.0876	61.36
98.50	4.5080	1.5088	65.37
98.50	1.9712	0.6590	65.30

The final point to be determined was the composition of the solid phase in equilibrium with the saturated solution. While working at temperatures of 50° and above, the samples taken deposited long monoclinic needles upon cooling, while samples taken at 30° deposited shorter monoclinic prisms, both forms having previously been described by Groos.[1] However, there seemed to be no definite temperature marking
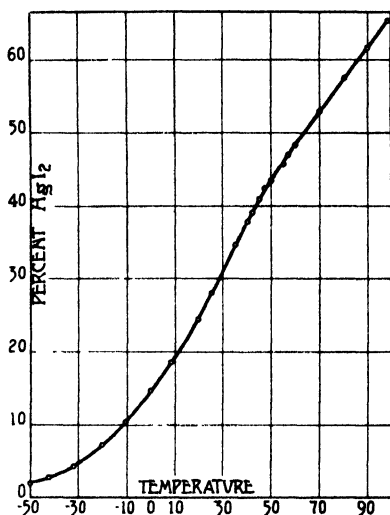
the transition from prisms to needles. For example, at 40° one sample deposited both needles and prisms, while at 35° one sample deposited needles and the other deposited prisms. Careful analyses of each variety of crystals showed the percentage content of mercuric iodide to be identical, namely, 74.15 percent. This corresponds very nearly to the theoretical mercuric iodide content for the compound $HgI_2.2C_5H_5N$, which is 74.18 percent.

Summary

The solubility of mercuric iodide in pyridine has been determined between —50° and +98.5°.

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[1] Archiv. Pharm., **228**, 73 (1890).

Only one compound of mercuric iodide and pyridine exists in equilibrium with saturated solution of mercuric iodide in pyridine between these limits, the compound being that previously described by Monari and others. This compound may appear either as long monoclinic needles or as shorter monoclinic prisms, as previously stated by Groos.

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ELECTROMOTIVE FORCES AND ELECTRODE PO-
TENTIALS IN PURE AND MIXED SOLVENTS. II

BY F. S. MORTIMER AND J. N. PEARCE

The first systematic study of the electromotive forces in non-aqueous solvents was made by Jones.[1] By using cells ·of the type:

$$Ag—AgNO_3.aq.—AgNO_3.non\text{-}aq.—Ag,$$

with the same concentration of the salt in each solvent, he had hoped to be able to calculate the degree of dissociation of the salt in the non-aqueous solvent. He found, however, that the solution pressure of a metal varies from solvent to solvent. By substituting the values found by Völlmer[2] for the degree of dissociation of silver nitrate in ethyl alcohol, he calculated the solution pressure of silver in ethyl alcohol to be about one-fortieth of the value which it has in pure water.

Kahlenberg[3] measured the electrode potentials of ten different metals in o.10 N solutions of their salts in about thirty different solvents. From his results he concludes that the solution pressure of a metal varies not only with the different solvents and their mixtures, but also with the nature of the dissolved salt.

The electrode potentials and electromotive forces of a number of cells containing solutions of salts of silver, lead, copper, mercury, cadmium and zinc were studied by Neustadt and Abegg.[4] For solvents they used water, methyl alcohol, ethyl alcohol, acetone and pyridine. In all cases, the half cell, $Ag—AgNO_3{}^-$, constitutes one-half of the cell. Since the potential differences in methyl alcohol, ethyl alcohol and acetone were found to be approximately equal to those in water,

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[1] Zeit. phys. Chem., **14**, 346 (1894).
[2] Dissertation, Halle (1892).
[3] Jour. Phys. Chem., **3**, 379 (1899).
[4] Zeit. phys. Chem., **69**, 486 (1910).

they believed that the solution pressures for any one metal in these four solvents are practically the same. The considerably lower values obtained for solutions in pyridine were attributed to an extremely low ionic concentration, due to association and the subsequent complex ionization of the silver nitrate in the pyridine solutions.

Getman[1] and Getman and Gibbons[2] have measured the potentials of cadmium and zinc in alcoholic solutions of their salts, using the normal calomel electrode as the other half of the cell. Since the electrode potentials were found to become more negative as the concentration of the salt increases, they conclude that the applicability of the Nernst equation is very improbable. In a later investigation[3] of the electrode potentials, transport numbers, and conductivities of solutions of silver nitrate in methyl alcohol, ethyl alcohol, acetone, and aniline, certain abnormalities were found which they attribute to the formation of complex solute-solvent compounds which dissociate more or less gradually with dilution.

The first attempt to measure the electromotive forces of concentration cells in alcoholic solutions were made by Wilson.[4] His cells contained silver nitrate dissolved in methyl and ethyl alcohol and the measurements were made at 0 and 25°. From the agreement between his results and the values calculated from the conductivities of the solutions he draws the conclusion that the Nernst equation can also be applied to non-aqueous solutions, yet admitting at the same time that the Nernst equation can hardly be recognized as giving more than approximate values.

Bell and Field[5] measured the electromotive forces of concentration cells in water and ethyl alcoholic solutions of silver nitrate. The electromotive forces of concentration cells in aqueous solutions at 25° were found to be in accord with the

[1] Am. Chem. Jour., 46, 117 (1911).
[2] Ibid., 48, 124 (1912).
[3] Jour. Am. Chem. Soc., 36, 1630 (1914).
[4] Am. Chem. Jour., 35, 78 (1906).
[5] Jour. Am. Chem. Soc., 35, 715 (1913).

Nernst equation for dilute solutions. Rearranging the equation for cells with transference to the form:

$$K = \frac{2v}{u+v} \cdot \frac{RT}{nf} \cdot \log_e 10 = \frac{E}{\log c_1/c_2},$$

where c_1 and c_2 are the concentrations of the cation in the two solutions, they calculated the values of K. The values thus obtained for the aqueous solutions varied between 0.0560 and 0.0623. For the ethyl alcoholic solutions the value of K for three combinations varied between 0.068 and 0.074. Assuming the value 0.0623 for aqueous solutions and 0.074 for alcoholic solutions, they calculated the transport number of the NO_3^- ion to be 0.523 and 0.62, respectively. Since the value of K varies so widely in these solvents, they conclude that the transport number of an ion is not independent of the concentration of the salt.

The first systematic study of electrode potentials and electromotive forces in mixed solvents was reported by Pearce and Farr.[1] They determined the electromotive forces of concentration cells and the electrode potentials of silver against its ions for solutions of silver nitrate in water, methyl alcohol and ethyl alcohol, and in their binary mixtures at both 0° and 25°. From the close agreement between the observed and calculated values for the electromotive forces it was shown that the Nernst equation can be applied not only to solutions in non-aqueous solvents, but also to solutions in the binary mixtures of these solvents. The electrode potentials were found to be relatively greatest in the methyl alcohol and smallest in the aqueous solutions, the corresponding values in ethyl alcohol occupying an intermediate position. In each solvent the electrode potential is highest in the most concentrated solution. These potential values decrease very rapidly with the first initial dilutions, while subsequently the decrease proceeds almost linearly as the concentration of the salt decreases. 'The electrode potentials in the binary mixtures of the alcohols obey the law of mixtures. In the binary mixtures

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[1] Jour. Phys. Chem., **18**, 729 (1914).

of water with the two alcohols the electrode potentials in-
crease slowly at first with the addition of the alcohol from the
value in pure water up to mixtures containing about seventy-
five percent of alcohol, and then more rapidly with further
increase in the proportion of alcohol. They also determined
the temperature coefficients of the electrode potentials, the
solution pressure of silver in each of the pure solvents, and
the heat of ionization in the pure solvents and in their fifty
percent binary mixtures.

In the hope that still further light may be thrown upon the
effect of solvent upon the electrochemistry of solutions, a
fourth solvent—pyridine—has been added to the series. As
a solvent pyridine occupies a position almost as unique as
that of water. Its molecular structure is very different from
that of the alcohols and water. It has a much lower dielectric
constant, yet many salts dissolved in it give solutions of fairly
good conducting power. The solution of salts in pyridine
is generally accompanied by the liberation of a considerable
quantity of heat. Salts crystallizing from pyridine solutions
often separate with from one to several molecules of pyridine.
Obviously, therefore, the salt molecules as well as the ions
must be solvated to a considerable extent in solution.

Materials and Solutions

Water.—The conductivity water used in making all of
the aqueous solutions was prepared according to the method
of Jones and Mackay.[1] It had a specific conductance of
$0.6 - 1.5 \times 10^{-6}$ mhos.

Ethyl Alcohol.—Ordinary 95 percent alcohol was allowed
to stand over fresh quick-lime for two or three weeks. It
was then decanted and distilled. The distillate was allowed
to stand over anhydrous copper sulphate for one week and
then redistilled. This distillate was refluxed with metallic
calcium for ten hours and again distilled. Finally, it was
refluxed for two hours with silver nitrate to remove aldehydes
and other reducing agents. The distillate from this treatment

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[1] Am. Chem. Jour., **19**, 83 (1897).

was collected and preserved in dry glass-stoppered bottles, being protected from the air during distillation by phosphorus pentoxide tubes. In each distillation a fractionating column was used and only that middle portion which passed over between 77.9° and 78° (uncor.) was retained.

Methyl Alcohol.—Kahlbaum's best grade was further purified in the same manner as the ethyl alcohol except that the treatment with quick-lime was omitted. Only that fraction of the distillate passing over between 64.9° and 65.1° was collected.

Pyridine.—The best grade of pyridine obtainable was allowed to stand over fused potassium hydroxide for several weeks. It was then decanted and distilled. That portion passing over between 115.3° and 115.7° was collected and preserved in small glass-stoppered bottles, protected during the distilling process by a train of phosphorus pentoxide tubes.

The solvent mixtures were made up on a percentage basis by weight, the weights of the separate solvent components being accurate to 0.1 gram per liter.

Silver Nitrate.—Baker's "Analyzed" salt was further purified by recrystallization from a hot saturated solution of the salt in conductivity water. The crystals were filtered on a Büchner funnel, washed with ice-cold conductivity water, sucked dry and then heated for several hours in a toluol bath at 109°. The salt when perfectly dry was kept in dark bottles further protected by dark cloths.

Potassium Chloride.—Baker's "Analyzed" salt was further purified by precipitating a saturated solution by hydrogen chloride gas. The precipitate was filtered, washed with conductivity water, and dried in an air bath at 110°. The salt was always strongly heated before using.

Mercury.—The mercury used in preparing the calomel electrodes was purified by usual nitric acid method and the acid completely removed by repeated washing with conductivity water. It was then distilled under reduced pressure in a current of dry air.

Calomel.—Kahlbaum's best grade of mercurous chloride

was washed repeatedly with a 0.10 N solution of potassium chloride after which it was preserved under a fresh sample of the same solution in dark bottles.

Solutions.—All solutions were prepared by direct weighing, or by the suitable dilution of freshly prepared solutions. They were made up to volume at 25°, and to avoid the possibility of decomposition occurring in the solutions, all electrometric measurements were made on the same day.

Apparatus

The apparatus used in this work was the same as that used by Farr.[1] The 0°-bath was obtained by clean, finely crushed ice moistened with distilled water. The 25°-bath was kept in rapid circulation by a motor-driven mechanical stirrer. It was electrically heated and maintained at 25 ± 0.01° by an electrically controlled temperature regulator.

Seven half-cells and two calomel electrodes were used simultaneously in this investigation. Each half-cell was fitted with a stopcock in the connecting tube. These were always kept closed except for very short intervals when measurements were being made. Loose plugs of filter paper inserted in the ends of the connecting tubes practically eliminated any possible diffusion even when the stopcocks were momentarily opened for potential readings. The middle vessel was so arranged that the connecting tubes of all the cells could be inserted simultaneously through tightly fitting rubber stoppers. With this arrangement the solutions were not unduly exposed and the measurements could be made on any combination by simply changing the wire leads and opening the stopcocks in the connecting tubes. A normal solution of ammonium nitrate was used in the middle vessel. It was assumed that this solution eliminates the diffusion potential.[2]

The calomel electrodes were prepared in the following manner: In the bottom of the electrode vessel was placed a large globule of mercury. This was next covered by an inti-

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[1] Loc. cit.

[2] Ostwald-Luther: Messungen, 3rd Ed., p, 448.

mately mixed paste of calomel and mercury moistened with 0.10 *N* solution of potassium chloride. Over this was placed a solution of 0.10 *N* potassium chloride which had been shaken with calomel and allowed to stand in contact with it until saturated. The single potential of the calomel electrode was calculated from the value given by Richards,[1] the values taken being +0.5986 volt at 0° and 0.6186 at 25°. These electrodes were renewed alternately every two weeks and were found to be immediately reproducible in most cases to within one-tenth of a millivolt. Upon standing for a day or longer they checked in every case to within 0.02 millivolt.

The electromotive forces were measured by means of a Wolff potentiometer in connection with a sensitive Leeds and Northrup "Type H" wall galvanometer. In aqueous solutions it was easily sensitive to 0.01 millivolt, but the high resistances in non-aqueous solutions made it impossible to detect differences of less than 0.1 millivolt. A Cadmium-Weston cell which had been recently standardized against a similar element certified by the Bureau of Standards was used as a standard of reference. It had an electromotive force of 1.01745 volts at 25°. While its temperature coefficient is practically negligible, it was kept at this temperature by insulating it in a deep beaker immersed in the 25°-bath.

The silver electrodes were prepared by fusing short pieces of silver wire into the ends of glass tubes. To the ends sealed into the glass were soldered copper wires, each the length of the glass tube. The tubes were then filled to within an inch of the top with hard paraffine which prevented the mercury, with which the contact was made, from amalgamating the silver electrode. Before using, the electrodes were plated by connecting them in series in a solution of potassium-silver cyanide. After a current of ten milliamperes had been passed for three hours, they were removed, rinsed with distilled water and then allowed to stand for forty-eight hours in contact with a button of pure silver under a pure aqueous solution of silver nitrate. Ten or twelve electrodes were thus prepared. The

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[1] Zeit. phys. Chem., **24**, 29 (1897).

choice of the electrodes to be used was made in the following way: They were all grouped in a single cell containing a 0.10 N solution of silver nitrate which was in turn connected with a calomel electrode through an intermediate solution of ammonium nitrate. Only those electrodes were chosen which gave identically the same electromotive forces with the calomel.

It was observed early in the work that the electrode potential of a freshly prepared half-cell changes on standing. This change for any given electrode is most rapid at first, the rate of change then gradually decreasing to zero at equilibrium. In order to eliminate any errors from this source the whole battery of half-cells with their respective electrodes and solutions was set up and allowed to stand for at least one and one-half hours at constant temperature. This interval was repeatedly found to be sufficient for the attainment of equilibrium between the electrode and the solution.

Theoretical

There are four sources of electromotive force in any cell: the thermo-electric potential at the junction of the wire leads with the electrodes, the diffusion potential at the junction of the two solutions, and the two electrode potentials at the surfaces of contact between the electrodes and their respective solutions. The first of these is entirely eliminated by compensation, and it is assumed that the diffusion potential has been made negligible by the interposition of the 1.0 N solution of nitrate. There are left for consideration, therefore, only the two electrode potentials.

According to the equation of Nernst, based on the osmotic theory of the cell, the electrode potential of a metal in contact with a solution of its ions is given by the expression

$$E = \frac{RT}{nF} \cdot \log_e \frac{P}{p}, \qquad \qquad (1)$$

where R represents the gas constant (1.985 cals.), T the absolute temperature, n the valence of the cation and F the faraday (96540 coulombs). P and p represent, respectively, the solution pressure of the metal and the osmotic pressure of

the cation in the solution, these pressures being measured in atmospheres.

Assuming the absence of a diffusion potential, the electromotive force (E) of a concentration cell is equal to the difference between the two electrode potentials, or

$$E = \frac{RT}{nF} \cdot \log_e \frac{p_1}{p_2}. \qquad (2)$$

Since the osmotic pressure of the ions is proportional to their concentrations, and since for normal electrolytes the ionic concentrations may be considered as approximately proportional to the equivalent conductivities of the solutions, then

$$\frac{p_1}{p_2} = \frac{\alpha_1 c_1}{\alpha_2 c_2} = \frac{\lambda_1 c_1}{\lambda_2 c_2},$$

where c, α and λ represent the concentration of the salt, the degree of dissociation and the equivalent conductance, respectively. By substitution in Equation 2, we obtain

$$E = \frac{RT}{nF} \cdot \log_e \frac{\lambda_1 c_1}{\lambda_2 c_2}. \qquad (3)$$

The temperature coefficients have been calculated by means of the relation

$$\frac{dE}{dT} = \frac{E_{25} - E_0}{25 \cdot E_{25}}. \qquad (4)$$

The relation between the electrical and chemical energies of a cell is given by the well-known Helmholtz equation, *viz.*,

$$E = \frac{Q}{F} + T \cdot \frac{dE}{dT}.$$

By rearranging this equation and multiplying by 0.2387 to transform joules into calories, we obtain the expression

$$Q = F \left(E - T \cdot \frac{dE}{dT} \right) \times 0.2337, \qquad (5)$$

where Q is the heat of ionization.

Assuming that the osmotic pressure of the ions is given by the expression

$$p = 22.4 \cdot c \cdot x \cdot \frac{T}{273},$$

the solution pressure of a metal may be calculated from a transformation of Equation 1, e. g.,

$$\log_e P = \frac{EnF}{RT} + \log_e \left(22.4 \cdot c \cdot \alpha \cdot \frac{T}{273} \right). \qquad (6)$$

Results

The results obtained are given in the following tables and curves:

TABLE I

Electrode Potentials in the Water-Pyridine Series

25°

N	100 W volts	75 W—25 P volts	50 W—50 P volts	25 W—75 P volts	100 P volts
1.0	1.0513	—[1]	0.7513	0.7002	0.6112
0.50	1.0430	0.7603	0.7026	0.6496	0.5866
0.10	1.0097	0.7075	0.6578	0.6070	0.5470
0.05	0.9944	0.6820	0.6371	0.5878	0.5367
0.025	0.9774	0.6650	0.6178	0.5714	0.5255
0.01	0.9578	0.6426	0.6023	0.5504	0.5066
0.005	0.9403	0.6343	0.5928	0.5328	0.4853

TABLE II

Electrode Potentials in the Water-Pyridine Series

0°

N	100 W volts	75 W—25 P volts	50 W—50 P volts	25 W—75 P volts	100 P volts
1.0	1.0456	—[1]	0.7282	0.6836	0.5810
0.50	1.0411	0.7332	0.6842	0.6361	0.5678
0.10	1.0095	0.7034	0.6324	0.5946	0.5296
0.05	0.9913	0.6739	0.6368	0.5758	0.5216
0.025	0.9820	0.6581	0.6085	0.5630	0.5081
0.01	0.9625	0.6405	0.5973	0.5421	0.4926
0.005	0.9471	0.6334	0.5866	0.5309	0.4746

Mean Temperature Coefficients of Electrode Potentials

| —0.000045 | +0.000430 | +0.000762 | +0.000771 | +0.001293 |

[1] Insoluble.

TABLE III
Electrode Potentials in the Ethyl Alcohol-Pyridine Series
25°

N	100 E volts	75 E—25 P volts	50 E—50 P volts	25 E—75 P volts	100 P volts
0.50	—[1]	0.7986	0.6872	0.6380	0.5866
0.10	1.0826	0.7348	0.6391	0.5921	0.5470
0.05	1.0686	0.7084	0.6222	0.5790	0.5367
0.025	1.0592	0.7007	0.6148	0.5655	0.5255
0.01	1.0391	0.6821	0.5906	0.5363	0.5066
0.005	1.0277	0.6684	0.5667	0.5204	0.4853

TABLE IV
Electrode Potentials in the Ethyl Alcohol-Pyridine Series
0°

N	100 E volts	75 E—25 P volts	50 E—50 P volts	25 E—75 P volts	100 P volts
0.50	—[1]	0.7698	0.6621	0.6190	0.5678
0.10	1.0696	0.7144	0.6195	0.5741	0.5296
0.05	1.0571	0.6866	0.6036	0.5603	0.5216
0.025	1.0466	0.6739	0.5952	0.5473	0.5081
0.01	1.0251	0.6583	0.5726	0.5108	0.4926
0.005	1.0131	0.6397	0.5512	0.5083	0.4746

Mean Temperature Coefficients of Electrode Potentials

| +0.000506 | +0.001457 | +0.001280 | +0.001295 | +0.001293 |

TABLE V
Electrode Potentials in the Methyl Alcohol-Pyridine Series
25°

N	100 M volts	75 M—25 P volts	50 M—50 P volts	25 M—75 P volts	100 P volts
0.50	—[1]	0.8105	0.7177	0.6386	0.5866
0.10	1.0975	0.7306	0.6541	0.5911	0.5470
0.05	1.0799	0.7145	0.6369	0.5690	0.5367
0.025	1.0707	0.6959	0.6201	0.5520	0.5255
0.01	1.0507	0.6766	0.6000	0.5426	0.5066
0.005	1.0286	0.6612	0.5834	0.5280	0.4853

[1] Insoluble.

TABLE VI
Electrode Potentials in the Methyl Alcohol-Pyridine Series
0°

N	100 M volts	75 M—25 P volts	50 M—50 P volts	25 M—75 P volts	100 P volts
0.50	—[1]	0.7811	0.6934	0.6175	0.5678
0.10	1.0916	0.7126	0.6233	0.5658	0.5296
0.05	1.0706	0.6970	0.6184	0.5522	0.5216
0.025	1.0611	0.6814	0.6017	0.5369	0.5081
0.01	1.0330	0.6628	0.5851	0.5243	0.4926
0.005	1.0167	0.6493	0.5614	0.5120	0.4746

Mean Temperature Coefficients of Electrode Potentials

+0.000368 | +0.000989 | +0.001419 | +0.001352 | +0.001293

TABLE VII
Heats of Ionization

Solvent	Electrode potential	Mean temperature coefficient	Heat of ionization	Dielectric constant
Water	1.0097	—0.000069	23728	80.5
75 W—25 P	0.7075	+0.000430	13352	56.9
50 W—50 P	0.6578	+0.000762	9925	41.1
25 W—75 P	0.6070	+0.000691	9243	31.5
Pyridine	0.5470	+0.001293	3726	11.2
Ethyl Alcohol	1.0826	+0.000506	21472	—
75 E—25 P	0.7348	+0.001457	6927	—
50 E—50 P	0.6391	+0.001280	5938	—
25 E—75 P	0.5921	+0.001354	4346	—
Methyl Alcohol	1.0975	+0.000415	22440	32.8
75 M—25 P	0.7306	+0.000989	10045	24.5
50 M—50 P	0.6541	+0.001420	5321	18.3
25 M—75 P	0.5911	+0.001356	4310	—

TABLE VIII
Solution Pressures in the Pure Solvents

Solvent	Solution pressure
Water	2.46×10^{-17}
Ethyl Alcohol	2.02×10^{-18}
Methyl Alcohol	3.55×10^{-19}
Pyridine	1.77×10^{-10}

[1] Insoluble.

Discussion

In the accompanying tables (I–VI) are given the potentials of the silver electrode measured against solutions of its ions in water, methyl alcohol, ethyl alcohol and pyridine, and in the binary mixtures of pyridine with each of the other solvents. From these tables and the corresponding curves (Plate II) it is to be observed that the electrode potentials of silver are much higher for solutions in water and the two alcohols than for equivalent concentrations in pyridine. Furthermore for any given concentration of silver nitrate the electrode potential increases with the decrease in the proportion of pyridine in the solvent mixture. This increase is very gradual until seventy-five percent of the pyridine has been replaced by the second solvent. For water-pyridine mixtures the initial increase is apparently a linear function of the percent of water present in the mixture. With further decrease in the proportion of pyridine there is a rapid increase in the value of the electrode potential up to its value in the second solvent.

These electrode potential-solvent curves show a striking resemblance to the dielectric constant-solvent curve plotted for the same solvent mixtures. The dielectric constants of the water-pyridine and methyl alcohol-pyridine mixtures were determined by the Drude-Schmidt method and the values are given in Table VII. In both mixtures the dielectric constant increases rather slowly at first with the decrease in the proportion of pyridine up to mixtures containing about seventy-five percent of the second solvent and then more rapidly with further decrease in the proportion of pyridine. According to the law of Dutoit and Aston those solvents which have the highest dielectric constants are those in which electrolytic dissociation takes place to the greatest extent. Thus for a given concentration of silver nitrate ionization should increase with a decrease in the pyridine content of the solvent mixture. For metals whose electrodes are electropositive to solutions of their ions this should mean a corresponding increase in the electrode potential, and such is the case in the solvents studied.

The curves for the water-pyridine series show also a

F. S. Mortimer and J. N. Pearce

striking resemblance to the curve obtained by Hartley, Thomas and Appleby[1] for the surface tention of the same series of mixtures. Whether or not any relation exists between surface tension and the electrode potential is a question still unanswered.

Volume
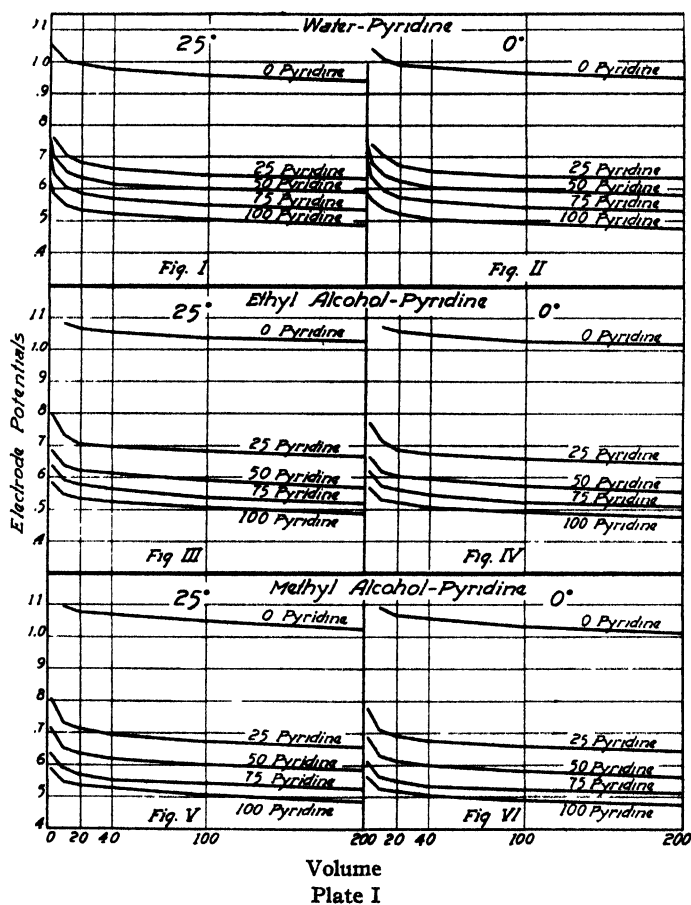
Plate I

For all solvents, simple and mixed, the electrode potentials increase with increasing concentration of the dissolved salt. From the curves (Plate I) it will be observed that, starting with the most concentrated solution, the electrode potential drops

[1] Jour. Chem. Soc., **93,** 549 (1908).

very rapidly with the first dilutions and then decreases almost linearly with the dilution in the more dilute solutions. It will also be observed from the volume-electrode potential curves for any set of binary mixtures and, hence, for all pure solvents as well, that the curves obtained are, within limits of experimental error, practically parallel with each other. This confirms the relation pointed out by Farr.[1] "If the electromotive force at the junction of the two solutions is entirely eliminated, and since the electromotive force of a concentration cell at a given temperature is proportional to the logarithm of the ratio of the ionic concentrations in the two solutions, it follows that the ratio between the ionic concentrations for equivalent concentrations of the salt in the separate solvents is constant and independent of the dilution."

The electromotive forces of all the possible concentration cells in each of the simple and mixed solvents were determined immediately after the readings for the electrode potentials had been made. The electromotive forces calculated for the concentration cells in the pure solvents—water, methyl alcohol and ethyl alcohol—agree closely with those determined by experiment. This confirms the statement made by Farr[1] that the Nernst equation does hold for concentration cells in these solvents.

For solutions in pure pyridine, however, the values calculated for the concentration cells from conductivity data do not even approximate the electromotive forces experimentally determined. For all concentration cells where the normal solution constitutes one-half of the cell, the calculated values are smaller, whereas when the concentrations in each of the half-cells are less than 0.5 N, the calculated values are larger than those observed. These deviations were not found to be appreciably lessened when the conductance values are corrected for viscosity. All of which goes to prove that, in so far as pyridine solutions are concerned, one of two conditions exist. Either the Nernst equation does not hold for concentration cells in pyridine as solvent, or the

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[1] Loc. cit.

electrical conductivity of these solutions is in no sense a measure of the degree of dissociation. Evidence seems to point most strongly to the latter condition as the one which is the cause of these deviations.

Walden and Centnerszwer,[1] using the boiling-point method, have found that the molecular weights of silver nitrate in dilute pyridine solutions are normal, while in the more concentrated solutions the molecular weight is greater than normal. This evidence of association does not necessarily exclude the presence of ionization. Since pyridine solutions show considerable conductivity, ions of some sort must be present. As was pointed out by Pearce[2] the amount of polymerization of the solute need only be very slight in order to compensate for the effect due to ionization. When these two effects just balance each other the molecular weights will appear as normal.

Transference measurements in pyridine solutions made by Neustadt and Abegg[3] showed that both the Ag^+ ion and the NO_3 radicle migrate toward the cathode. They assumed that, if ionization does take place, it does so according to the equation

$$(AgNO_3)_2 = \overset{+}{Ag_2}(NO_3) + \overset{-}{NO_3}.$$
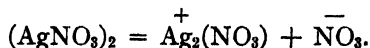
That the simple Ag^+ ions are also present is not to be doubted. In all probability we are here dealing with a complex equilibrium, *viz.*, the simple and polymerized solute molecules in equilibrium with each other and with their respective ions. Under such conditions it would be impossible to calculate the electromotive forces from conductivity data.

The temperature coefficients of the electrode potentials have been calculated for solutions in the pure and mixed solvents and they are inserted at the bottoms of the tables for the electrode potentials. Obviously the accuracy of the temperature coefficients depend to a large extent upon the

[1] Zeit. phys. Chem., **55**, 321 (1906).

[2] Jour. Phys. Chem., **19**, 30 (1914).

[3] Zeit. phys. Chem., **69**, 486 (1910).

accuracy attained in the potential measurements, a slight error in the latter being enormously enhanced when it appears in the temperature coefficient. All of the temperature coefficients are positive except those in the more dilute aqueous solutions. At concentrations slightly greater than
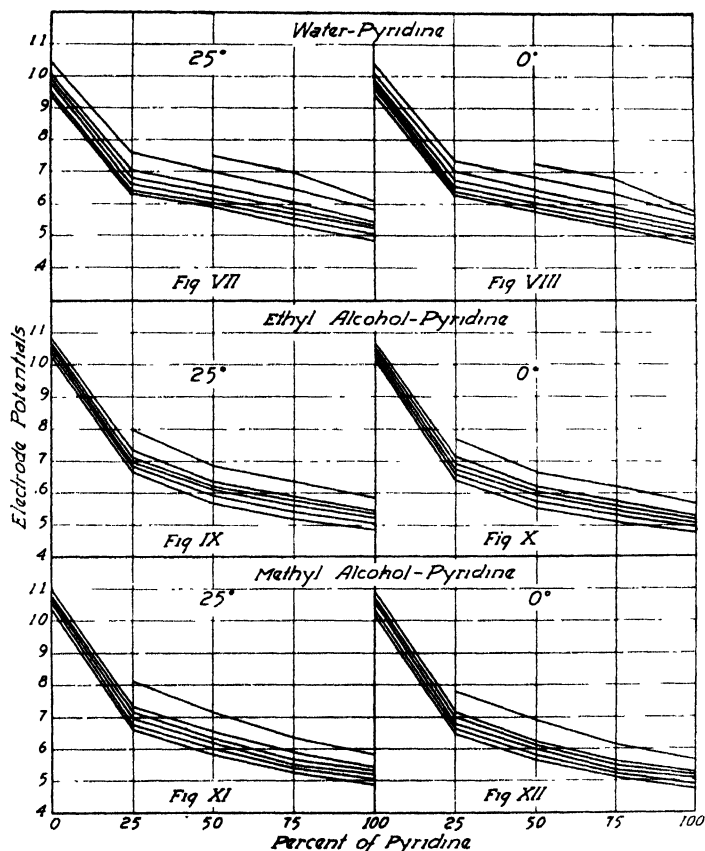
Plate II

o.10 *N* the temperature coefficients in the aqueous solutions become positive. In all solutions containing pyridine the temperature coefficients are extraordinarily high. In the water-pyridine series they increase regularly from the value in pure water up to the value in pure pyridine. In the methyl alcohol-pyridine series these coefficients increase rapidly to

a maximum value in the fifty percent solvent mixture, then decrease slowly to the value in pyridine.   A similar relation is found for the binary mixtures of ethyl alcohol and pyridine except that the maximum occurs in the presence of a smaller percent of pyridine.

The heats of ionization are given in Table VII.   They were calculated by substituting the mean temperature coefficients and the corresponding electrode potentials of the o.10 N solutions in Equation 5.   The heat of ionization of silver in pyridine is relatively very low.   For any series of solvent mixtures the heat of ionization decreases the most rapidly upon the first addition of pyridine to the second solvent, and then more slowly as the percent of pyridine is increased. The heat of ionization decreases with increase in the proportion of pyridine relatively more rapidly in each of the alcoholic pyridine series than in that of water and pyridine.

In the last column of Table VII are inserted a few dielectric constants.[1]   Here again it will be observed that the first addition of pyridine to the second solvent produces relatively the greatest change in the dielectric constant.

The solution pressure of silver in contact with pyridine solutions of silver ions is found to be much higher than when in contact with aqueous or alcoholic solutions.   These pressures were calculated by making the proper substitutions in Equation 6, using in each case the value of the electrode potential found for the o.10 N solutions.   The values of α were calculated from the following conductivity data:

Solvent	λ_{10}	λ_∞
Water	94.96[2]	128.54[3]
Methyl alcohol	38.58[2]	98.00[4]
Ethyl alcohol	13.21[2]	35.60[3]
Pyridine	27.58[5]	71.00[5]

[1] Determined by Mr. Richard Beeson, Drude-Schmidt method.
[2] Jones and Bassett: Am. Chem. Jour., **32,** 409 (1904).
[3] Kohlrausch, Sitzungsber. Berl. Akad., **26,** 570 (1902).
[4] Vollmer: Loc. cit.
[5] H. L. Dunlap (this laboratory).

The solution pressures in water and the alcohols are in good agreement with those calculated by Farr.[1] The value calculated for water is also very close to the value, 2.3×10^{-17}, found by Neumann. Assuming from conductivity data that silver nitrate is only one-fourth as highly ionized in pyridine as in water solutions, Kahlenberg calculated the solution pressure of silver in pyridine to be 3.4×10^{-10}. The value found in this work is 1.77×10^{-10}.

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[1] Loc. cit.

THE ELECTRICAL CONDUCTANCE OF SEVERAL SALTS IN PYRIDINE

BY J. HOWARD MATHEWS AND ALFRED J. JOHNSON

This paper constitutes a further contribution to a detailed study of the physical chemistry of pyridine and its solutions which has been under way in this laboratory for a number of years.

Laszczynski and Gorski[1] determined the electrical conductance of lithium chloride, and the iodides and sulphocyanates of potassium, sodium and ammonium in pyridine at a temperature of 18° C. They found that the equivalent conductance at infinite dilution could be calculated by extrapolation from the equivalent conductance curves, in some cases. Lincoln[2] found that a large number of inorganic salts yielded conducting solutions, but that the equivalent conductance at infinite dilution could be determined in but a few cases only. Dutoit and Duperthuis[3] studied the conductance of potassium iodide, potassium sulphocyanate and sodium sulphocyanate in pyridine for dilutions ranging from 1,000 to 20,000 liters per gram-mole of salt. It was found that Ostwald's dilution law held in most cases, rendering it possible to calculate the degree of dissociation at any given dilution. Hevesy[4] worked on the electrolysis of pyridine solutions of the iodides of barium, strontium and calcium and found that these salts dissolved fairly well in pyridine yielding solutions that were good electrolytes.

Anderson[5] has recently made a careful, systematic study of the conductance of fifteen different inorganic salts in pyridine over as wide a range of concentration as the experimental conditions would allow, and at three different tempera-

[1] Zeit. Elektrochemie, 4, 290–293 (1897).
[2] Jour. Phys. Chem., 3, 459–484 (1899).
[3] Jour. Chim. phys., 6, 699–725 (1909).
[4] Zeit. Elektrochemie, 16, 672 (1911).
[5] Jour. Phys. Chem., 19, 753–789 (1915).

tures, *viz.*, 0°, 25° and 50° C.   From the data thus obtained
the temperature coefficients were calculated.   It was found
that in general distinct minima in the temperature coefficients
occurred, while in the case of lithium bromide, sodium iodide,
cobalt chloride and cadmium nitrate, negative temperature
coefficients were encountered at certain dilutions.   Two
classes of electrolytes were observed: (1) those for which the
equivalent conductance increased throughout, and (2) those
which gave minimum values.   The value of the equivalent
conductance at infinite dilution is given for lithium iodide at
0°, 25° and 50°; for sodium iodide at 0°, and for potassium
sulphocyanate at 0°.

In the present work, which was under way when Ander-
son's article appeared, the electrical conductance of six salts
was determined at 25°, and of two of them at 0°.

For measuring conductance, the Kohlrausch method
was used.   An excellent Wheatstone bridge with ten ratio
coils, made by Leeds and Northrup, was employed, together
with an induction coil and a special tuned "wireless" telephone
receiver to which an ordinary physician's stethoscope was
attached for the purpose of concentrating the sound from the
telephone receiver.[1]   The ratio coils of the Wheatstone bridge
were guaranteed by the manufacturer to be accurate to within
$1/_{50}$ of one percent and the resistance coils to within $1/_{25}$ of
one percent.

An Arrhenius conductivity cell, with a ground-glass
stopper and sealed-in electrodes, was used.   The electrodes
were covered with a velvety coating of platinum black, pro-
duced by electrolyzing a solution containing 3 grams of
platinic chloride and 0.02–0.03 gram of lead acetate in 100
cc of water, reversing the current every half minute for 10–15
minutes, using a current of such strength that a moderately
rapid evolution of gas was obtained.   The platinizing solution
was then removed and replaced by a dilute solution of sul-
phuric acid and the current passed for about 15 minutes with

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[1] For this suggestion and the loan of the receiver we are indebted to Pro-
fessor Acree of the U. S. Forest Products Laboratory.

reversal of current every minute. This treatment removed the platinizing liquid and occluded chlorine from the platinum coatings. The electrodes and conductivity vessel were then washed thoroughly, first with warm, distilled water and finally with conductivity water until all soluble matter had been removed. A 0.02 N potassium chloride solution was used in determining the cell constant. Chemically pure potassium chloride was recrystallized from conductivity water and carefully dried at a temperature just below red heat. The specific conductance of the 0.02 N solution of potassium chloride was taken as 0.002768 at 25° C and 0.001522 at 0° C. The cell constant at 25° was 0.170.

A 50 cc flask, calibrated at room temperature, was used in making the original solutions. In running a series of measurements, exactly 20 cc of the solution were placed in the conductivity cell and after the temperature of the bath had been attained the resistance was measured. A pipette calibrated to take up exactly 10 cc was then used to remove one-half of the solution and a second pipette calibrated to deliver 10 cc was used to replace the volume removed by fresh pyridine, thus giving a solution of one-half the concentration of the original. This process of dilution was repeated as long as fairly accurate measurements of conductivity could be made.

For the measurements made at 25° an electrically controlled thermostat was used. A regulator entirely filled with mercury was substituted for the ordinary toluene filled regulator, with excellent success. The variation in temperature in this thermostat was not greater than ±0.01° C. For measurements at 0° a large Dewar flask filled with clean, crushed ice moistened with distilled water was used. A cork lined with tin-foil was used as a cover and the conductivity cell and thermometer were fitted into holes bored through the cork.

The pyridine was purified by allowing it to stand over fused electrolytic caustic potash for several weeks, with an occasional shaking, and was then decanted off and digested for several hours with potassium permanganate and barium

oxide (prepared by fusing barium dioxide) under a reflux condenser.[1] It was finally decanted off and distilled, the fraction distilling between 114.5–115.3° C at 730 mm being used. By this method of purification pyridine having an average specific conductance of 0.74 × 10⁻⁷ was obtained. This is the same value as that obtained by Anderson.

In the following data, V denotes the volume of the solution, in liters, containing one gram-equivalent weight of the salt, and L_o and L_{25} represent the equivalent conductance of the solutions at 0° and 25° C, respectively. Two separate series of determinations were made for each salt. The temperature coefficient was calculated according to the customary

formula: $\dfrac{L_{25} - L_o}{L_o \times 25}$.

In the curves which follow, the cube roots of the volumes in liters are plotted as abscissae and the equivalent conductances corresponding as ordinates.

Lead Nitrate

Lead nitrate was purified by recrystallizing twice from conductivity water and drying at a temperature of about 120° C. The conductances of solutions varying in concentration from $N/4$ to $N/2048$ were measured in duplicate series.

TABLE I

V	Conductance at 25° C			Conductance at 0° C			
	Series I	Series II	L_{25} Mean	Series I	Series II	L_o Mean	Temp. coeff.
4	0.0501	0.0507	0.0504	—	—	—	—
8	0.0728	0.0734	0.0731	0.052	0.052	0.052	0.0162
16	0.0930	0 0933	0.0932	0.072	0.071	0.072	0.0117
32	0.1263	0.1267	0.1265	0.110	0.105	0.108	0.0070
64	0.1840	0.1843	0.1842	0.157	0.158	0.158	0.0066
128	0.2655	0.2668	0.2661	0.243	0.238	0.241	0.0040
256	0.4201	0.4211	0.4206	0.386	0.384	0.385	0.0037
512	0.6467	0.6476	0.6472	0.631	0.629	0.630	0.0022
1024	1.032	1.034	1.033	1.001	1.003	1.002	0 0008
2048	1.676	1.686	1.681	1.660	1.672	1.666	0.0003

[1] Wilcox: Jour. Phys. Chem., **14,** 576 (1910).

Walton and Judd[1] have determined the temperature-solubility curve for lead nitrate in pyridine, for temperatures between —19.4° and 110° C. Three crystalline modifications were observed, *viz.*, $Pb(NO_3)_2.4C_5H_5N$, $Pb(NO_3)_2.3C_5H_5N$, and $3Pb(NO_3)_2.2C_5H_5N$.

From Fig. I it is seen that the equivalent conductance of
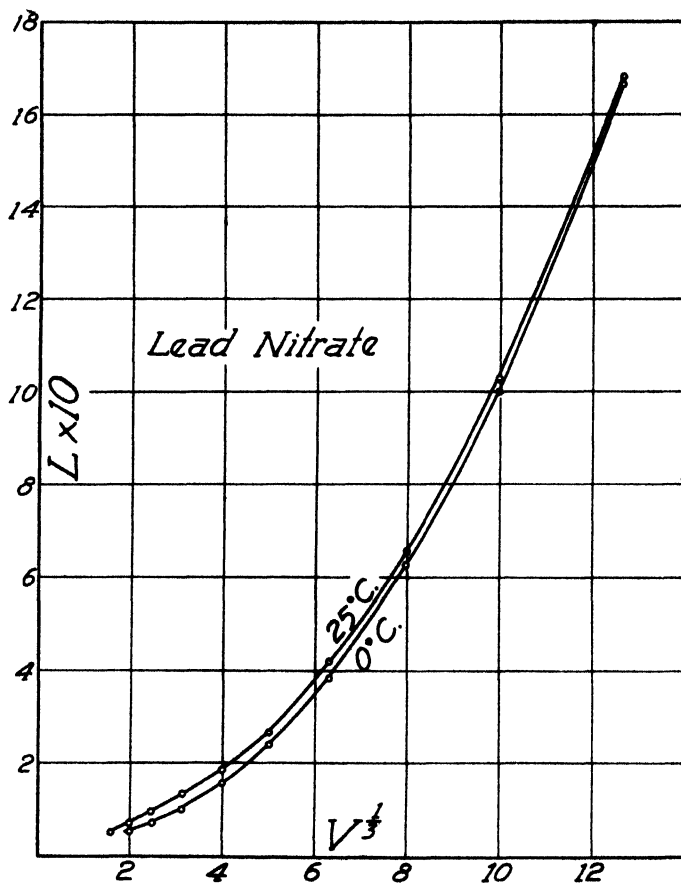
Fig. I

lead nitrate at first increases rapidly on dilution, but as the dilution increases there is a less rapid increase. However,

[1] Jour. Am. Chem. Soc., **33**, 1026 (1911).

there is no approach to a maximum value in the dilutions studied. The equivalent conductance at $0°$ is a little less than at $25°$ and, as the table shows, the temperature coefficient decreases with dilution.

Copper Acetate

Anhydrous copper acetate was obtained by recrystallizing copper acetate several times from pyridine and carefully driving off the pyridine from the crystalline copper acetate-pyridine compound thus formed.

TABLE II

V	Conductance at $25°$		
	Series I	Series II	L₂₅ Mean
64	0.0228	0.0227	0.0228
128	0.0398	0.0400	0.0399
256	0.0638	0.0641	0.0639
512	0.0957	0.0963	0.0960
1024	0.1468	0.1477	0.1473
2048	0.2145	0.2152	0.2148
4096	0.3025	0.3020	0.3023
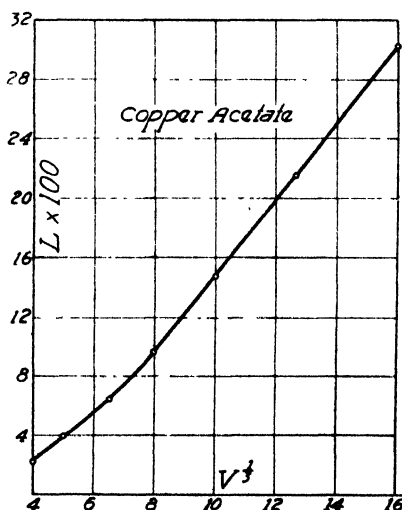
Fig. II

Fig. II shows that the conductance increases with dilution through the range of the determinations made, without the attainment of a maximum value. Mathews and Benger[1] determined the temperature-solubility curve for copper acetate in pyridine at temperatures ranging from —11.6° to 95° C and proved the existence of two compounds, $Cu(C_2H_3O_2)_2.$- $4 C_5H_5N$ and $Cu(C_2H_3O_2)_2.C_5H_5N$, having a transition point at 44.7° C.

Silver Sulphate

The silver sulphate used was purified by recrystallizing twice from redistilled water and drying at a temperature of 105° C. Silver sulphate is a good conductor of electricity in a pyridine solution. Conductivity measurements were made at two temperatures, 0° and 25° C.

TABLE III

V	Conductance at 25°			Conductance at 0°			
	Series I	Series II	L_{25} Mean	Series I	Series II	L_0 Mean	Temp. coeff.
64	1.19	1.19	1.19	—	—	—	—
128	1.48	1.47	1.48	1.00	0.99	1.00	0.0192
256	1.91	1.93	1.92	1.54	1.53	1.54	0.0099
512	2.70	2.68	2.69	2.36	2.34	2.35	0.0058
1024	3.86	3.86	3.86	3.62	3.61	3.62	0.0027
2048	5.67	5.63	5.65	5.58	5.60	5.59	0.0004
4096	8.65	8.62	8.64	8.30	8.32	8.31	0.0016
8192	12.98	12.97	12.98	12.21	12.19	12.20	0.0026
16384	19.27	19.29	19.28	16.40	16.40	16.40	0.0070
32768	29.62	29.61	29.62	20.19	20.20	20.20	0.0186
65536	45.10	45.09	45.10	24.38	24.42	24.40	0.0339

Deemer[2] determined the solubility-temperature curve of silver sulphate in pyridine for temperatures from —20° to 70° C and proved the existence of the compound $Ag_2SO_4.$- C_5H_5N between the temperatures —19° and 7° C.

[1] Jour. Phys. Chem., **18**, 264 (1914).
[2] Thesis, M.S., U. of W., 1914.

The curves (Fig. III) show that at 25° the conductance rises rapidly with dilution, while at 0° there is a considerable falling off in the rate of increase in the more dilute solutions.
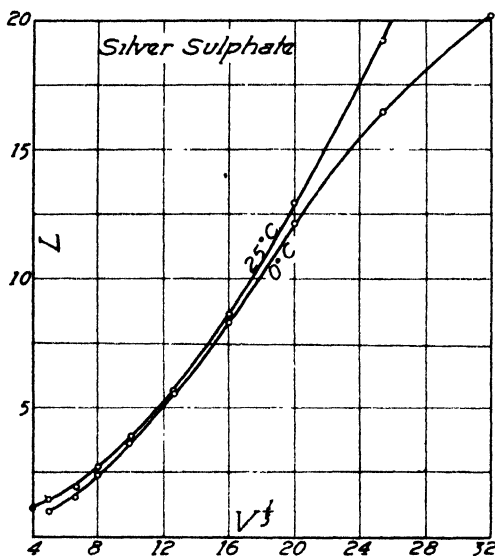
Fig. III

The temperature coefficient decreased with dilution until a dilution of 2048 liters had been obtained, when it increased with about the same rapidity with which it had decreased.

Silver Sulphocyanate

Cotton[1] determined the solubility curve of silver sulphocyanate in pyridine for temperatures between -20° and 110° C and proved the existence of four silver sulphocyanate-pyridine compounds, *viz.*, $AgCNS.C_5H_5N$, $4AgCNS.3C_5H_5N$, $2AgCNS.-C_5H_5N$ and $4AgCNS.C_5H_5N$.

Silver sulphocyanate was prepared by adding a solution of potassium sulphocyanate to a solution of silver nitrate, working in a dark room. The precipitated salt was washed thoroughly by decantation with water, followed by purified alcohol and finally with purified ether, bringing the precipitate

[1] Thesis, M.S., U. of W., 1911.

upon a filter with the last portion of ether. In this way it was possible to dry the silver sulphocyanate very rapidly by heating slightly to drive off the ether and then drying at a temperature of 60° for some time. Silver sulphocyanate in pyridine is a good conductor of the electric current.

TABLE IV

V	Conductance at 25°		
	Series I	Series II	L$_{as}$ Mean
4	2.05	2.05	2.05
8	1.96	1.95	1.96
16	1.92	1.92	1.92
32	1.93	1.93	1.93
64	2.04	2.04	2.04
128	2.28	2.29	2.29
256	2.76	2.80	2.78
512	3.56	3.54	3.55
1024	4.63	4.62	4.63
2048	6.28	6.27	6.28
4096	8.47	8.43	8.45
8192	11.51	11.49	11.50
16384	15.78	15.76	15.77
32768	21.80	21.78	21.79
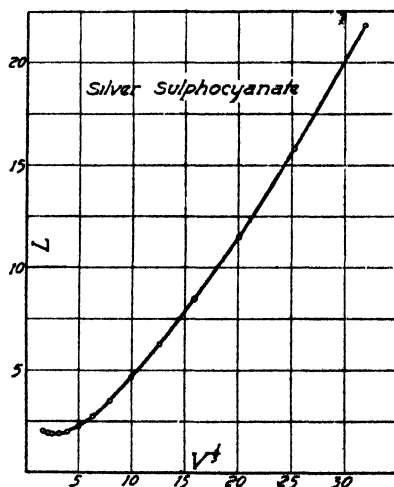
Fig. IV

From the curve (Fig. IV) it is seen that the conductance decreases in the more concentrated solutions, while in the dilute solutions the increase in conductance is very rapid, with no tendency toward the attainment of a constant maximum value.

Silver Cyanide

Silver cyanide was prepared by adding potassium cyanide solution to a solution of silver nitrate, washing with water, alcohol and ether as in the case of the sulphocyanate. The salt yields a fairly good conducting solution in the more concentrated solutions, but the increase in equivalent conductance with dilution is not very great. The curve obtained (Fig. V) resembles the one obtained by Anderson[1] for ammo-
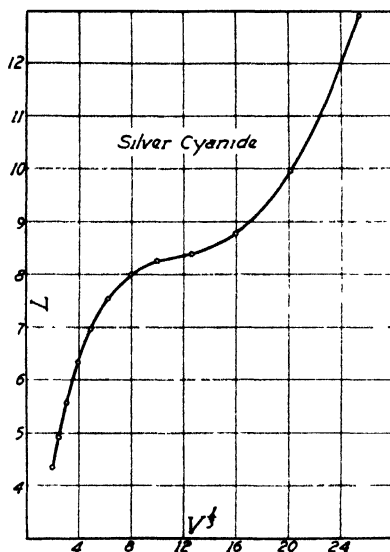
Fig. V

nium sulphocyanate. The equivalent conductance curve rises rapidly at first, then becomes almost parallel with the X-axis and again rises.

[1] Loc. cit.

TABLE V

V	Conductance at 25°		
	Series I	Series II	L̄as Mean
8	4.35	4.35	4.35
16	4.92	4.93	4.93
32	5.57	5.57	5.57
64	6.31	6.31	6.31
128	6.95	6.93	6.94
256	7.53	7.53	7.53
512	8.01	7.99	8.00
1024	8.26	8.25	8.26
2048	8.37	8.35	8.36
4096	8.79	8.77	8.78
8192	9.95	9.91	9.93
16384	12.20	12.18	12.19

Franklin[1] found an analogous relation in the conductance values for ammonium sulphocyanate and tetramethylammonium iodide in liquid sulphur dioxide. He found that the molecular conductance first increased to a maximum, then fell to a minimum value and finally approached the usual maximum on further dilution. He explained these results by assuming that the dissociated salt is "auto-ionized" in the concentrated solutions and that this effect decreases with dilution. On the other hand, the decrease in viscosity with dilution causes a rise in ionic mobility. These two effects were assumed to balance each other at the first maximum. On further dilution the "auto-ionization" disappeared and the conductivity from then on is due to the dissociating power of the solvent.

Silver Chloride

Silver chloride was prepared by adding hydrochloric acid to a solution of silver nitrate. The precipitated silver chloride was washed thoroughly by means of hot water by decantation, and finally on a filter. The washed silver chloride was then carefully dried at 110° C. All of these operations were carried

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[1] Jour. Phys. Chem., **15**, 675–697 (1911).

out in a dark room. Kahlenberg and Wittich[1] have determined the temperature-solubility curve of silver chloride in pyridine between —56° and 110° C. Two crystalline phases were observed: (1) $AgCl.2C_5H_5N$ and (2) $AgCl.C_5H_5N$, with a transition point at about —21°. At —1° there is another transition point, between $AgCl.C_5H_5N$ and AgCl.

TABLE VI

V	Conductance at 25°		
	Series I	Series II	L_{25} Mean
16	0.986	0.986	0.986
32	1.201	1.201	1.201
64	1.462	1.461	1.462
128	1.733	1.731	1.732
256	1.994	1.992	1.993
512	2.229	2.225	2.227
1024	2.388	2.382	2.385
2048	2.538	2.532	2.535
4096	2.710	2.700	2.705
8192	2.998	2.991	2.994
16384	3.420	3.410	3.415
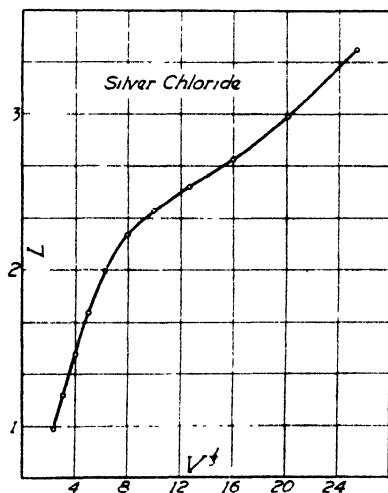
Fig. VI

[1] Jour. Phys. Chem., 13, 427 (1909).

From the curve (Fig. VI) it is seen that silver chloride is a fairly good conductor, but that the increase in equivalent conductance in dilute solutions is not very rapid. No maximum value is approached, however, in the dilutions used. There seems to be some tendency in moderately dilute solutions, where the curve bends slightly toward the X-axis, to act in a way similar to silver cyanide.

Fig. VII shows all of the preceding conductance curves
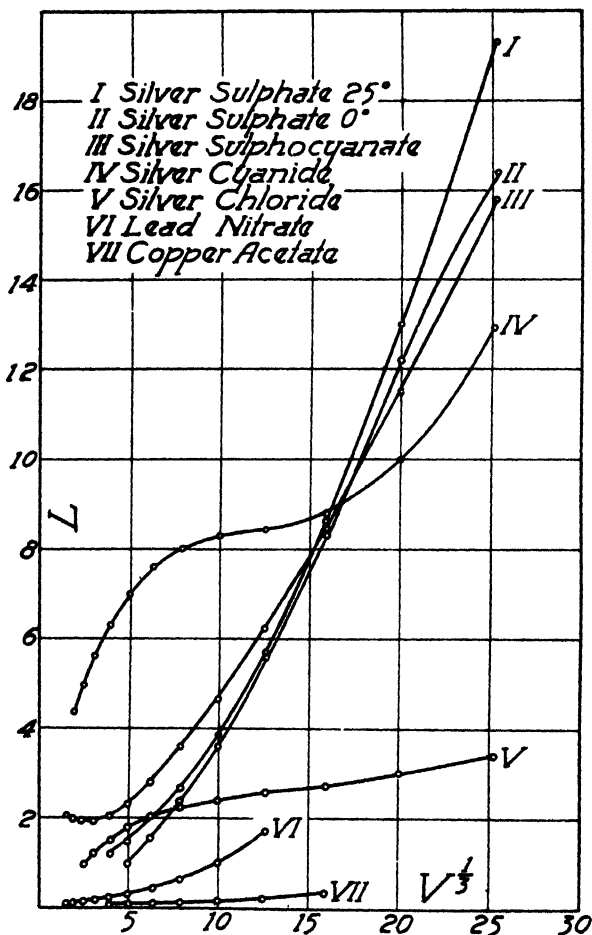
Fig. VII

plotted on the same scale, and, therefore, gives an interesting graphic comparison of the magnitude of the conductances as well as their behavior on dilution.

According to the modern theory of electrolytic dissociation the electrical conductance of an electrolyte is dependent upon the number of ions present in solution, their velocities and the charges they carry. The number of ions in solution is determined by the degree of dissociation of the dissolved electrolyte and according to the Nernst[1]-Thomson[2] rule the dissociating power of a solvent is greater the greater the dielectric constant of the liquid. The velocity of the ions is dependent in some measure on the viscosity of the solution and on their mass or volume. The mass or volume of either or both ions may be further augmented by combination with molecules of the solvent to form more or less highly solvated ions. Franklin[3] in attempting to apply the Arrhenius dissociation theory to explain the decrease in molecular conductance with increasing dilution assumes that the decrease is due to a decrease in "auto-ionization" which more than compensates for the increase in molecular conductance due to a decrease in viscosity.

Sachanov[4] studied the molecular conductance of various solutions in acetic and propionic acids and in aniline, methylaniline and dimethylaniline and found that the molecular conductance decreased in nearly every case with dilution and he came to the conclusion[5] that a decrease in molecular conductance with increasing dilution is just as characteristic for solvents with low dielectric constants as is an increase in molecular conductance in solvents with high dielectric constants. He asserts that electrolytic dissociation does not depend solely upon the magnitude of the dielectric constant, but also on the solvates and complex ions. The formation of such ions favors

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[1] Zeit. phys. Chem., **13**, 531 (1894).

[2] Phil. Mag., **36**, 320 (1893).

[3] Loc. cit.

[4] Jour. Russ. Phys. Chem. Soc., **42**, 683 (1910); **43**, 526 (1911); **44**, 324 (1912).

[5] Zeit. phys. Chem., **80**, 13 (1912).

electrolytic dissociation because the electro-affinity of these complex ions is greater than that of the simple ions. In solvents with low dielectric constants, he says, only the complexes which yield cómplex ions of high "electro-affinity" can undergo electrolytic dissociation. The decrease in equivalent conductance in such solvents is explained as being due to the formation of these polymerized solute molecules on dilution.

In 1901, Schlundt[1] published a set of exceptions to the Nernst-Thomson rule and showed conclusively that this rule could not be held in the light of the facts presented. Mathews[2] continued and verified the work of Kahlenberg[3] on the sulphocyanates and mustard oils, in which it was found that solutions of trichloracetic acid in the mustard oils were poor conductors, notwithstanding the fact that the mustard oils have fairly high dielectric constants and, hence, should give good conducting solutions. These poorly conducting solutions of trichloracetic acid nevertheless acted rapidly upon carbonates and metals, which according to the theory of electrolytic dissociation should occur only in conducting solutions. The dielectric constants of a considerable number of liquids were determined and it was found that the exceptions to the Nernst-Thomson rule were as numerous as the confirmations. The work of Eggers[4] on dielectric constants led to similar conclusions.

Anderson[5] divides the salts which he studied into two types: First, those which give minimum conductance values at certain dilutions, such as the mercuric halides and copper nitrate. Second, those like the nitrates of silver and cadmium, the chlorides of lithium and sodium, lithium bromide, and the thiocyanates of potassium and ammonium, which upon dilution give increasing values of equivalent conductance. Anderson attempts to show that the phenomenon of decreasing equivalent conductance with increasing dilution is due entirely to the presence and properties of the polymerized

[1] Jour. Phys. Chem., **5**, 157, 503 (1901).

[2] Ibid., **9**, 641 (1905).

[3] Zeit. phys. Chem., **46**, 64 (1903).

[4] Jour. Phys. Chem., **8**, 14 (1904).

[5] Loc. cit.

solute molecules which are present in solutions showing this phenomenon. He gives equations representing the possible equilibria in the case of mercuric chloride at different concentrations, between the simple and polymerized molecules of mercuric chloride, the simple and complex ions and the solvated ions and molecules.

Anderson explains the minima of temperature coefficients (which phenomenon he states is quite general in pyridine solutions) on the basis of viscosity and ionic solvation. Briefly his arguments are as follows: In the more concentrated solutions the pyridine held on as pyridine of solvation would be at a maximum and the effect of the decrease in complexity of the solvates due to a rise in temperature would be to increase the amount of the pure solvent. This would mean a decrease[1] in the viscosity of the solution which would be augmented by the decrease in viscosity of the pure solvent due to a rise in temperature. The solvated ions, which may or may not have been altered appreciably, due to rise in temperature, are able to migrate more rapidly. In the less concentrated solutions the viscosity changes due to a rise in temperature will be less pronounced. Hence, the value of the temperature coefficients will decrease. With the decreasing viscosity changes upon dilution, the ionic solvation increases. The instability of the solvated ions with rise in temperature is also increasing with dilution. As the temperature is raised the decrease in complexity of the solvated ions will cause an increase in their mobility. Thus the solvated-ion effect may annul that of the viscosity and it is this condition which gives rise to the minimum temperature coefficients. As the increase in dilution continues the ion-solvation effect becomes the sole factor and, hence, a steady increase in the values of the temperature coefficients is obtained.

Granting the correctness of the views stated above, it would seem that the factors affecting electrical conductance of salts in pyridine are numerous and complicated, and difficult of determination by experimental means. It is very

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[1] This is not necessarily the case, however.

evident that attempts to explain the behavior of solutions of various salts in pyridine on the basis of the Arrhenius theory of electrolytic dissociation become quite involved and cumbersome. Furthermore, it seems impossible to give an explanation which will hold, in principle, in every case; exceptions and anomalies show up wherever generalizations are attempted. Obviously, by arbitrarily putting together a suitable combination of simple and polymerized molecules, simple and polymerized ions, more or less solvated simple or complex molecules, more or less solvated simple or complex ions, in conjunction with unproven concepts concerning the dielectric constant, viscosity, ionic velocities, etc., and their relationship to conductance, it is possible to give an "explanation" of any conductance phenomenon. These explanations are as yet purely hypothetical (as far as pyridine solutions are concerned), since the experimental evidence to corroborate such assumptions is unfortunately lacking. In fact, the only foundation for these assumptions is the evident desire to harmonize the facts with the Arrhenius theory.

Summary

A study of the equivalent conductance of six salts in pyridine has been made at a temperature of 25° C and for some of them at 0°.

Several classes of electrolytes are to be observed: (1) those for which the equivalent conductance curve rises rapidly in the more concentrated solutions and shows some promise of becoming asymptotic in the more dilute solutions; (2) those for which the conductance increases more rapidly in the dilute solutions; (3) those which give minimum values of equivalent conductance; (4) those which show an irregularity in their equivalent conductance curves.

A resumé of some of the more recent explanations of the anomalies found in electrical conductance of salts in pyridine in attempts to make the Arrhenius theory of electrolytic dissociation apply has been given.

Laboratory of Physical Chemistry
University of Wisconsin
January, 1917

AN IMPROVED MERCURY STILL

BY L. H. DUSCHAK AND S. O. SPENCER[1]

The mercury still, shown in the accompanying diagram, embodies the principle of the familiar Weinhold apparatus, which by certain additions has been adapted to the distillation of mercury in the presence of a small partial pressure of oxygen as recommended by Hulett. Under this condition the common metals contaminating the mercury are oxidized and separated much more effectively than by ordinary distillation.[2]

The mercury after a preliminary cleansing by one of the usual methods, if necessary, is placed in the cup A with a reserve supply in the reservoir B by which the level in the cup is automatically maintained. By closing the stopcock this reservoir may be filled periodically without interrupting the distillation. The bore of this stopcock should be at least 5 mm so that air bubbles entering the bottom of the delivery tube will have no difficulty in passing. The horizontal branch of the three-way stopcock C is joined to a water aspirator, or other vacuum supply of moderate capacity. This stopcock may be also used for the rapid admission of air to the apparatus when it is desired to stop the distillation quickly.

When the vacuum is applied, mercury rises in the annular space between the extended neck of flask D and the condenser tube within. This flask will ordinarily have a capacity of 1,000 to 1,500 cc and may be of soda lime glass, although Pyrex or Jena glass is preferable. The flask is supported by an ample wooden clamp, not shown in the sketch, which grips the neck just below the gas burner. The elevation of the flask above the cup should be such that the difference in

[1] Published by permission of the Director, U. S. Bureau of Mines.

[2] Hulett: Phys. Rev., **33,** 307 (1911); Hulett and Minchin: Ibid., **21,** 388 (1905).

mercury levels will be 20 to 30 mm less than the mean baro-
metric pressure.
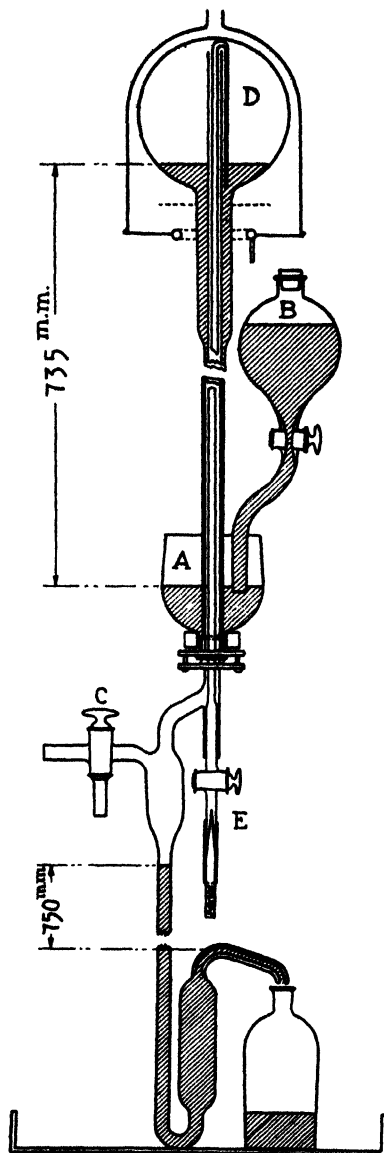
A very small stream of air enters the apparatus through the capillary tip at E. This is carefully adjusted so that several bubbles per second pass up through the mercury in D and a plug of cotton wool prevents dust from altering the size of the orifice. The rate of distillation is so regulated that the condensation of the mercury vapor in the upper part of tube F is practically completed 10 to 15 cm above the mercury level in the cup A. This may be judged by noting the temperature of the a s c e n d ing mercury column and also observing the formation of gas bubbles next the outer glass tube, which occurs only in the zone of condensation. With the apparatus in our laboratory the rate of distillation is about 750 g per hour.

In starting the apparatus it is obviously necessary either to close the lower end of tube F, or to introduce enough pure mercury to establish a barometric column. When the still has once been used sufficient mercury remains in the reservoir at the bottom for this purpose.

From time to time it is necessary to remove the flask D in order to wash out the accumulated dirt with nitric acid. To do this it is only necessary to loosen the clamp referred to above, and slip the flask off the condenser tube F, using care to avoid breaking the tiny capillary above.

As the still shown in the sketch is heated by gas a piece of nichrome gauze and an asbestos hood are used to insure symmetrical heating, but an electric heater as described by Hulett[1] can be equally well applied. With a dependable source of vacuum the apparatus is entirely automatic in operation.

The supports for the cup A, reservoir B, and flask D and the clamp for holding the stopper in the bottom of cup A should be robust and designed with due regard to the weight of mercury to be supported.

Bureau of Mines Experiment Station
Berkeley, California

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[1] Loc. cit.

THE EFFECT OF ADSORPTION ON THE PHYSICAL CHARACTER OF PRECIPITATED BARIUM SULPHATE

BY HARRY B. WEISER

In connection with a general discussion of the physical character of precipitates, Foulk[1] says:

"Some compounds readily separate in coarse heavy crystals and some do not. With the same precipitate the constituent in excess often has a marked influence. This is seen in the case of barium sulphate which comes down in much better form when precipitated with SO_4 than when Ba is in excess. Magnesium ammonium phosphate is also coarser when magnesium is in excess than under the reverse conditions. There is no explanation of this to offer.

"The presence in solution of substances taking no part in the reaction probably in all cases influences the character of the precipitate. In one or two cases this influence is marked as is shown by the precipitation of barium sulphate with SO_4. A large excess of hydrochloric acid favors this precipitation. When the reverse conditions obtain, however, and the precipitation is made with Ba in excess, a large amount of acid causes the precipitate to settle in a finely divided state."[2]

It is a well-known fact that precipitated barium sulphate is contaminated to a greater or lesser extent by substances present in the solution from which the precipitate forms. In many cases the degree of contamination is sufficiently great to affect materially the estimation of barium or of sulphate by the barium sulphate method. A quantitative study of the contamination with barium chloride, of the barium sulphate obtained in the precipitation of barium chloride by sulphuric acid and sulphuric acid by barium chloride has been

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[1] "Quantitative Chemical Analysis," 46 (1914).
[2] Cf. Foulk: Jour. Am. Chem. Soc., 18, 793 (1896).

made by Richards and Parker,[1] and by Hulett and Duschak.[2] The latter investigators find that barium chloride is taken up not only during precipitation but also when finely divided crystals of barium sulphate are suspended in a solution of barium chloride. As an explanation of the phenomenon they consider the possible formation of complex salts, such as $BaCl.HSO_4$ and $(BaCl)_2SO_4$.[3] Schneider[4] has investigated quantitatively the contamination of barium sulphate by ferric sulphate and Creighton[5] has made a similar study of the contamination with aluminum sulphate. Both investigators regard the phenomenon as a case of solid solution. The work of Küster and Thiel[6] and of Korte[7] who has repeated and extended Schneider's experiments, indicates that the phenomenon is a case of adsorption. In accord with this conclusion Vanino and Hartl[8] find that barium sulphate acts as an effective adsorption agent toward certain colloidal solutions in which it is placed. An extensive quantitative investigation of the various factors affecting the purity of barium sulphate precipitates has been made more recently by Allen and Johnston[9] and by Johnston and Adams,[10] and has led to the following conclusion: "Since the size of the crystal particles depends upon the degree of supersaturation, it follows that the degree of fineness of the particles is increased by a rapid addition of the precipitant; is diminished by precipitating in a medium in which barium sulphate is more soluble; and is further diminished when the precipitate remains in contact with a medium in which it is soluble by the process of recrystallization, the rate of which depends on this solubility.

[1] Zeit. anorg. Chem., **8**, 413 (1895).
[2] Ibid., **40**, 196 (1904).
[3] Cf. Folin: Jour. Biol. Chem., **1**, 131 (1905).
[4] Zeit. phys. Chem., **10**, 425 (1892).
[5] Zeit. anorg. Chem., **63**, 53 (1909).
[6] Ibid., **19**, 97; **22**, 424 (1899).
[7] Jour. Chem. Soc., **81**, 1503 (1905).
[8] Ber. deutsch. chem. Ges., **37**, 3620 (1904).
[9] Jour. Am. Chem. Soc., **32**, 588 (1910).
[10] Ibid., **33**, 829 (1911). Cf. also Kato and Noda: Mem. Coll. Sci. Eng. Kyoto, **2**, 217 (1909–10); Jour. Chem. Soc., **98** II, 895 (1910).

Now these are precisely the conditions which affect the occlusion, when the precipitates are made from identical solutions. We are, therefore, justified in concluding that this occlusion is a phenomenon of adsorption at the surface of the grains of the precipitate; and that its amount depends upon (*a*) the composition of the original solution, and (*b*) the initial fineness of the precipitate and the amount of recrystallization which has taken place.

"This explanation, besides accounting for our own results also accords with those of Richards and Parker and Hulett and Duschak......"

Since barium sulphate shows a marked tendency to adsorb many other substances, the presence of such substances in a solution from which barium sulphate is precipitated will have a peptizing effect on the salt[1] that will act independently of the above quoted factors to produce small particles. Since adsorption is a specific property, other conditions being identical, we should expect to get the most finely divided particles when barium sulphate is precipitated in the presence of substances for which the salt shows the greatest specific adsorption. As a matter of fact this is exactly what was found to be the case.

It is a well established fact that a solid salt shows a distinct preferential adsorption for its own ions. The writer has shown in a recent article[2] that lead molybdate possesses such a marked adsorption for molybdate ion that in the presence of this ion lead molybdate is peptized to such a degree that a stable colloidal solution is formed. Bancroft[3] has called attention to a large number of cases of this kind. Of particular interest is the case of the silver halides. By the addition of a slight excess of alkali halide to silver nitrate Lottermoser[4] prepared a colloidal solution of silver halide

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[1] Bancroft: "The Theory of Peptization," Jour. Phys. Chem., **20, 85** (1916).

[2] Jour. Phys. Chem., **20,** 640 (1916).

[3] Ibid., **20,** 97 (1916).

[4] Jour. prakt. Chem., [2] **68,** 341 (1903); **72,** 39 (1905); **73,** 374 (1906); Zeit. phys. Chem., **62,** 371 (1908).

that owed its stability to the adsorbed halogen ion, since it moved to the anode under electrical stress. By adding a slight excess of silver nitrate to the alkali halide a colloidal solution of silver halide was again prepared; but this time the colloid owed its stability to adsorbed silver ion since it moved to the cathode under electrical stress.

Analogous to the behavior of the silver halides, it might be expected that under the right conditions a colloidal solution of barium sulphate could be prepared, peptized by preferential adsorption of barium ion or of sulphate ion. It is evident that Kato's[1] colloidal solution of barium sulphate was peptized by adsorbed barium ion. This colloid prepared by the intermixing of alcoholic solutions of sulphuric acid and barium acetate was positive. Cations of higher valency hindered the coagulation. Barium chloride and barium nitrate did not cause coagulation except in highly concentrated solutions and the presence of barium ion hindered the coagulation by potassium chloride.

The fact that the interacting substances were mixed in stoichiometric proportions does not change matters since we know that barium ion is so strongly adsorbed that it is always present in barium sulphate precipitates even in the presence of an excess of soluble sulphate.[2] Moreover, precipitation is complete only after a very long time, if at all, when neither ion is in excess.

Recoura[3] has prepared stable colloidal solutions of barium sulphate by double decomposition employing pure glycerol as the solvent for the reacting substances. A particularly stable variety was made using ethylate of barium and sulphuric acid. Recoura's colloidal solutions possessed properties similar to Kato's. Boiling coagulated them as did the addition of aqueous solutions of metallic salts with the exception of mercuric salts and the salts of barium. The presence of barium salts

[1] Mem. Coll. Sci. Eng. Kyoto, **2**, 187 (1909–10); Jour. Chem. Soc., **98** II, 850 (1910).

[2] Hulett and Duschak: Loc. cit.

[3] Comptes rendus, **146**, 1274 (1908).

increased the stability to a very marked extent, so that certain electrolytes which caused coagulation in the absence of an excess of barium ion had little coagulating effect in the presence of an excess of this ion. It is evident that the colloids adsorbed barium ion strongly and were stabilized thereby.

Under suitable conditions it should be possible to prepare a colloidal solution of barium sulphate stabilized by preferential adsorption of sulphate ion. This has been done in my laboratory by Mr. H. M. Bulbrook. The method used was similar to that of Recoura except that water and glycerol in the proportion of 1 to 5 was used as the solvent instead of pure glycerol. A tenth normal solution of barium chloride was mixed with a small excess of a tenth normal solution of sodium sulphate. A fairly stable colloidal solution resulted that was found to be negative since it moved to the anode under electrical stress. The apparatus employed in determining the direction of migration was similar to that recommended by Taylor.[1] It was essentially a glass U-tube with arms 14 cm in length made from thin-walled glass tubing of 3 mm internal diameter. A filling tube at the side joined the U-tube from below at a point midway between the arms. Just below the junction the side tube was constricted to a very narrow opening. To the top of the side tube was attached a small funnel by means of a rubber tube supplied with a screw clamp. To fill the apparatus a portion of the colloid was first poured into the funnel, after which the screw clamp was opened allowing it to fill the side tube completely. Any part of the solution which escaped into the U-tube was thoroughly washed out with distilled water. Water was then placed in the U-tube to a depth of 7 to 8 centimeters and the small electrodes were inserted at the top. The screw clamp was next carefully opened, allowing the solution to flow equally into the two arms until the electrodes dipped into the water. By this process a sharp dividing line between the colloid and water was obtained. A voltage between 125 v. and 150 v. was employed. The migration was slow but the direction was unmistakably

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[1] "The Chemistry of. Colloids," 78 (1915).

toward the anode.   In a half hour the water in the anode compartment became cloudy as much as 2 cm above the interface, while the interface in the cathode compartment remained almost as sharp as at the outset of the experiment.

In order to study the variable effect of an excess of certain ions on the physical character of precipitated barium sulphate, it is necessary to maintain certain conditions as nearly constant as possible.   In the precipitation of sulphuric acid by barium chloride and barium chloride by sulphuric acid, hydrochloric acid is one of the reacting products. Inasmuch as barium sulphate is slightly soluble in this acid,[1] its presence even in very slight amount will have some effect on the crystal size of the precipitated salt.   By precipitating the same weight of salt this effect will be the same irrespective of which ion is in excess.   In like manner when the precipitation is the result of the interaction of a barium salt and a sulphate, the soluble salt formed may have a slight solvent action that will be constant for the same weight of precipitate. Practically constant conditions of precipitation may be maintained by very rapid mixing of constant volumes of the reacting substances at constant temperature   The precipitation will be practically instantaneous in every case because of the very great insolubility of barium sulphate, particularly in the presence of an excess of barium ion or sulphate ion.   A very rapid and at the same time thorough mixing of the two reacting solutions is difficult to obtain.   In an investigation of factors affecting the crystal size of precipitated lead chromate, Free[2] attempted to avoid incomplete mixing by pouring one solution into another stirred by an electrically driven stirrer; but his results were not very satisfactory.   A simple apparatus was accordingly designed for the purpose that gave consistent and satisfactory results.   The apparatus, a diagram of which is shown in Fig. I, consists essentially of two concentric glass tubes.   The outer tube A is 2.7 cm internal diameter and 32 cm long; the inner one B is 2.1 cm external diameter, 1.9 cm

[1] Banthisch: Jour. prakt. Chem., **29,** 54 (1884).

[2] Jour. Phys. Chem., **13,** 114 (1909).

internal diameter and 36 cm long. To increase the efficiency
of the mixing, four small projections C are made on the lower
end of B. The tubes are supplied with the rubber stoppers
D and E; the former is held firmly in place in a hole bored
concentrically in the latter. For the purpose of heating the
apparatus it is suspended in the steam jacket F by means of
the cork G.

The method of using the apparatus was as follows:
After thorough cleaning, it was hung in the steam jacket at
least 20 minutes before use so that the tem-
perature of the solutions subsequently added
would not be reduced. Into one compart-
ment was poured 50 cc of a boiling solution
of barium salt, and into the other 50 cc of a
boiling solution of sulphuric acid or sulphate.
The volume of the compartments was such
that the level of the liquids in each was the
same. The apparatus and contents were next
removed from the steam bath and clamped
in an upright position. By a gentle twist
the inner tube was loosened and rapidly with-
drawn until the lower end was level with the
column of liquid. Immediately thereafter
the tube was again plunged into the liquid and
the process repeated a half dozen times or
more. In the wake of the rapidly with-
drawn tube flowed the solution from the outer
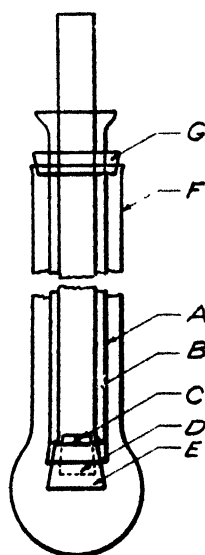
Fig. I

compartment and mixed with the outflowing solution from the
inner compartment, throughout the full length of the column
of liquid. The churning motion given to the inner tube im-
mediately after its withdrawal ensured complete mixing in
case this was not accomplished by the single operation. By
the manner of bringing the long narrow columns of liquid to-
gether, complete mixing was almost assured and the process
was as nearly instantaneous as one could wish.

After effecting the precipitation as above described, the
solution and precipitate were poured into a 200 cc beaker and

set aside. After half an hour the precipitate was stirred up, a drop of the supernatant liquid placed on a slide and a photomicrograph taken, by means of which it was possible to compare the character of the precipitates obtained under different conditions. For this purpose a Reichert metallurgical microscope was employed.

Since the more finely divided the particles of a precipitate the slower it will settle, it was thought that the relative sizes of the particles of precipitated barium sulphate obtained under different conditions could be determined by comparing the turbidities of supernatant solutions which had stood a definite length of time. Inasmuch as turbidity determinations give only a very approximate measure of the bulk of material in suspension, it was decided to draw off the supernatant liquid after a given interval of time, centrifuge out and measure the bulk of the precipitate. The actual procedure was as follows: Exactly 20 cc of a tenth normal solution of one of the salts were always taken and mixed with a measured excess (25 cc or 40 cc) of a tenth normal solution of the other salt. By this means the amount of precipitate was kept constant in all the experiments. The solutions were made up to 50 cc, heated to boiling, placed in the mixing apparatus, and mixed as previously described. The solution with precipitate was set aside and was well stirred at 20-minute intervals. After exactly one hour the solution was made up to 100 cc, stirred thoroughly and placed in a second apparatus to settle. This apparatus was simply a large test tube, 2.1 cm in diameter and 32 cm long, with an outlet tube 4 cm from the bottom. The outlet tube was bent sharply upward about 3 cm and then downward. This provision was necessary in order to prevent a portion of the precipitate from settling in the outlet tube. If any settled at the edge of the opening, it was readily dislodgèd by tapping with a rubber-covered rod. A tip was attached to the lower end of the outlet tube by a piece of rubber tubing and the opening was closed by a screw clamp. Before placing the suspended precipitate in the settling apparatus the exit tube was filled with distilled water. The

apparatus with contents was clamped in a vertical position and adjusted exactly by the aid of a small spirit level. A stop-watch was started at the moment the sample was poured into the apparatus and the settling was allowed to proceed exactly 15 minutes, after which the outlet tube was opened and the cloudy supernatant liquid was run into a beaker or measuring flask.

Since the bulk of barium sulphate in the supernatant liquid obtained as above described was never very large, the centrifuging was carried out in a 100 cc Goetz phosphorus tube, the capillary tube at the bottom of which was about 3 cm long and 1 mm internal diameter. This was sufficiently large to hold all of the suspended particles when barium chloride was precipitated in the presence of excess sulphuric acid but in other cases it was not. In the latter event, the supernatant liquid was run into a measuring flask, diluted to the mark and a suitable quantity pipetted for centrifuging. Before centrifuging the sample was diluted to approximately 100 cc, heated to boiling and set on the steam plate for 24 hours. By this digestion the particles were rendered somewhat larger and the volume of liquid was reduced to a few cubic centimeters. The precipitate was transferred quantitatively to the Goetz tube, using as little water as possible. The centrifuging was done in an electrically driven centrifuge making 1500 to 1600 revolutions per minute. The particles of barium sulphate precipitated in the presence of an excess of barium ion were so fine that difficulty was experienced in getting the last trace dislodged from the wall of the tube and thrown into the capillary. To accomplish this as nearly as possible, the centrifuging was continued for 15 minutes, stopping every two minutes to shake the solution thoroughly. It was unnecessary to take any such precautions when sulphate ion was in excess but the time of centrifuging was the same. The length of the column of precipitate was measured accurately with a cathetometer.

Particular precaution must be taken to keep the apparatus thoroughly clean. Each time before use every part was

brushed with a tube brush to remove any films of adhering barium sulphate, cleaned with chromic acid cleaning solution, and finally washed and rinsed with distilled water. By taking all necessary precautions results were obtained that are quite consistent throughout. Experiments were made with the constituent in excess in two different concentrations, *viz.*, one-fourth more and once more than the stoichiometric quantity. The results are recorded in Table I. Under "Solutions Taken" is given the volumes of solutions taken and diluted to 50 cc, so that the total volume after mixing was always 100 cc. Under "Length of column of BaSO₄" is recorded the bulks of barium sulphate held in suspension by a constant volume of solution obtained as above described, in terms of the length of a column of the salt 1 mm in diameter.

TABLE I

Solutions taken		Length of column of BaSO₄ (centimeters)			
$N/10$ H_2SO_4	$N/10$ $BaCl_2$	1	2	3	Mean
20	25	11.20	11.52	11.40	11.37
20	40	12.95	13.40	13.85	13.36
25	20	1.79	1.77	—	1.78
40	20	2.28	2.31	—	2.30
$N/10$ K_2SO_4	$N/10$ $BaCl_2$				
20	25	6.76	6.68	6.10	6.48
20	40	9.76	10.04	—	9.90
25	20	3.52	3 48	3.64	3.54
40	20	3.96	4.04	—	4.00
$N/10$ $MgSO_4$	$N/10$ $BaCl_2$				
20	25	7.32	7.92	—	7.62
20	40	9.88	10.44	9.60	9.97
25	20	2.49	2.58	—	2.54
40	20	2.99	3.02	—	3.01

That the figures in the above table represent with considerable accuracy the relative bulks of salt held in suspension

and, therefore, the relative degrees of fineness of the particles obtained under the specific conditions described, is shown clearly in a photograph of some samples of the supernatant liquid taken before centrifuging. This photograph is reproduced in Fig. II. The samples of supernatant liquids in the respective test tubes were obtained by mixing the solutions recorded in Table II.
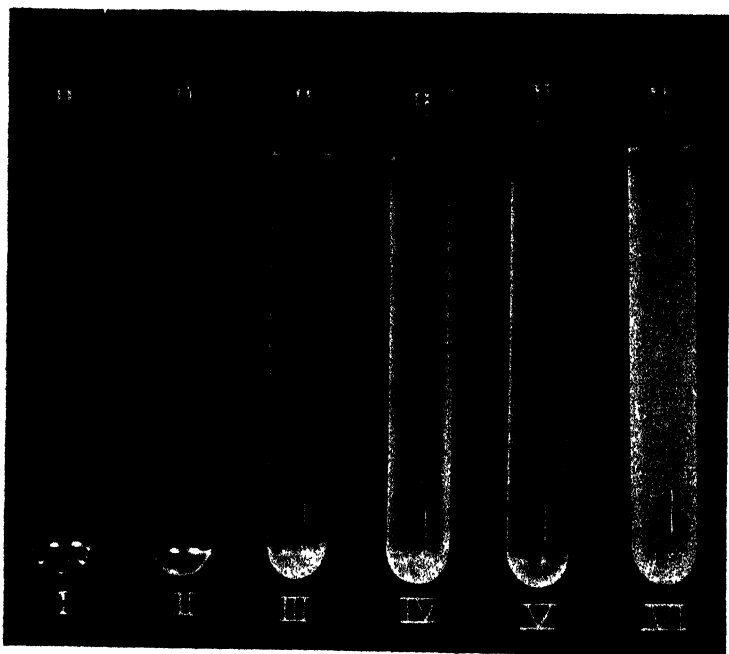
Fig II

TABLE II

Test-tube No.	Solutions taken		Length of column of $BaSO_4$ cm
I	Pure water		0.00
II	20 cc $N/10$ $BaCl_2$ 25 cc $N/10$ H_2SO_4	1 cc HCl, Conc.	0.56
III	20 cc $N/10$ $BaCl_2$ 25 cc $N/10$ $MgSO_4$	—	2.54
IV	20 cc $N/10$ $BaCl_2$ 25 cc $N/10$ K_2SO_4	—	3.54
V	20 cc $N/10$ $BaCl_2$ 25 cc $N/10$ H_2SO_4	—	1.78
VI	25 cc $N/10$ $BaCl_2$ 20 cc $N/10$ H_2SO_4	—	11.37

Fig III

Fig. IV

Figs. III and IV are photomicrographs of barium sulphate precipitates obtained as described by precipitating, respectively, sulphuric acid in the presence of one-half more than the theoretical quantity of barium chloride and barium chloride in the presence of one-half more than the theoretical quantity of sulphuric acid. The magnification is 180 diameters. In accord with the other facts observed it is evident that the precipitate formed in the presence of excess barium ions is distinctly the more finely divided.

Discussion of Results

Analogous to Lottermoser's colloidal solutions of the silver halides, it has been shown that under the right conditions colloidal solutions of barium sulphate may be formed that owe their stability in part at least to strong adsorption either of barium ion or of sulphate ion. Since this is the case, it is to be expected that the presence of either of these ions in excess will have an effect on the physical character of precipitated barium sulphate unless the effect is neutralized[1] by the presence of an equally strongly adsorbed ion of opposite charge.

Consider first the conditions that obtain when a solution of barium chloride in slight excess is mixed with a solution of sulphuric acid. In the presence of an excess of barium ion the precipitation is practically complete so that the only anion remaining is monovalent chlorine which is relatively slightly adsorbed. Of the cations barium ion is very strongly adsorbed and hydrogen ion is usually much more strongly adsorbed than most cations.[2] Under these conditions we should expect to get finely divided particles which is in exact accord with all the experimental data. A part of the barium chloride resulting from the partial neutralization of adsorbed barium ion by chlorine ion is retained by the precipitate in every case. This salt adsorption likewise tends to peptize the precipitate.

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[1] Bancroft: Jour. Phys. Chem., 19, 363 (1915).
[2] Freundlich: Kapillarchemie, 354 (1909).

Different conditions obtain when the precipitation takes place in the presence of excess sulphuric acid. Sulphate ion is relatively strongly adsorbed and would exert a peptizing action on the precipitate in the absence of a strongly adsorbed cation. In the presence of hydrogen ion, however, the adsorption of sulphate ion is cut down and larger particles are obtained in this case than in the previous one (compare Experiments 1 and 2 with 3 and 4, Table I; Tube VI with Tube V, Fig. II; Fig. III with Fig. IV). If the precipitation were effected with a sulphate in excess the cation of which is not so strongly adsorbed as hydrogen ion, *e. g.*, potassium sulphate, the strongly adsorbed sulphate ion would not be so completely neutralized and the precipitate should be more finely divided. This conclusion was confirmed (compare Experiments 7 and 8 with 3 and 4, Table I; Tube IV with Tube V, Fig. II). By substituting magnesium sulphate for potassium sulphate the precipitate obtained appeared somewhat less finely divided (compare Experiments 11 and 12 with 7 and 8, Table I; Tube III with Tube IV, Fig. II). This is what we might expect since, as a rule, divalent ions are adsorbed more strongly than univalent ones. This does not necessarily conflict with the observation of Hulett and Duschak[1] and Allen and Johnston[1] that magnesium sulphate is adsorbed by barium sulphate less strongly than potassium sulphate. Since adsorption is a specific property there is no *necessary* connection between the amount of adsorption of non-dissociated salt[2] and one of its separate ions.

The fact that the crystals are more finely divided with potassium sulphate than with sulphuric acid in excess might be attributed to the difference in solubility of the precipitate in potassium chloride and hydrochloric acid, the respective products of the reaction. If this were the case we should get a less finely divided precipitate with sulphuric acid than with potassium sulphate when barium chloride is in excess. As a matter of fact the reverse of this is true (compare Experiments

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[1] Loc. cit.
[2] Cf. Richards: Zeit. anorg. Chem., **23**, 383 (1900).

1 and 2 with 5 and 6, Table I), a result that is in exact accord with what we should expect since the concentration of barium ion is the same in each case, and hydrogen ion is adsorbed more strongly than potassium ion.

The next question considered was the effect of the presence of hydrochloric acid on the character of precipitated barium sulphate. At the beginning of this paper I called attention to the observations of Foulk. In the precipitation of barium with excess sulphuric acid Mar[1] recommends the use of an excess of hydrochloric acid for the purpose of securing large particles. In one set of experiments, 0.5 g of barium chloride in 400 cc was precipitated with 10 cc of dilute sulphuric acid (1 to 3) in the presence of varying amounts of hydrochloric acid. "When only one or two cubic centimeters of hydrochloric acid were present, the precipitate appeared immediately in a milky condition and settled slowly; as the amount of acid was increased, a point was soon reached where the precipitate was not so quickly apparent, but settled out much more quickly and in a coarser condition. With 10 cm³ to 15 cm³ of strong hydrochloric acid in the solution, the precipitate settled clear in ten or twelve minutes and was in excellent condition for filtration. When the solution contained 50 cm³ of the acid, the precipitate settled clear in five minutes. Upon adding the sulphuric acid to such very acid solutions, no precipitate shows for a moment, but then it separates in beautiful crystalline condition and falls almost immediately. It can be filtered with or without pressure in ten minutes." Mar believes that the solvent action of even large amounts of hydrochloric acid is insufficient to interfere with the estimation of barium by this method.

Browning[2] made similar observations on the effect of nitric acid and aqua regia. "The entire work would seem to show that the presence of an excess of nitric acid or aqua regia amounting to 10 per cent by volume of the liquid treated is not only not to be avoided in estimating barium as the

[1] Am. Jour. Sci., **41**, 288 (1891).
[2] Ibid., **45**, 399 (1893).

sulphate, but is actually beneficial. Ordinarily the advantage is found in the tendency of the precipitate to fall coarsely crystalline under the conditions."

Richards and Parker[1] have shown that the amount of barium chloride adsorbed is enormously increased by the presence of an excess of hydrochloric acid and point out that the accurate values obtained by Mar and by Browning are the result of a compensation of errors; the solubility in the presence of considerable excess of free acid is offset by the increase in the amount of barium chloride adsorbed. In the determination of sulphate Huybrechts[2] recommends the presence of 20 to 30 cc of 5 N hydrochloric acid in 500 cc of solution and definitely states that the error due to adsorption and to solubility compensate. In sulphate determinations, Folin[3] prescribes as safe limits of acidity 1 to 4 cc of concentrated hydrochloric acid in 150 cc of solution. Textbooks of analytical chemistry, however, generally recommend that the solution contain but little free hydrochloric acid both in the precipitation of sulphate by barium and the reverse. Allen and Johnston[4] used one of two acid concentrations, *viz.*, 2 cc of 2 percent or 1 cc of 20 percent hydrochloric acid in a volume of 350 cc. "The stronger acid has the advantage that the precipitates formed in its presence are somewhat denser and more convenient to handle, but the weaker acid is to be recommended because the sum of the corrections in that case is smaller."

In a method for the exact determination of sulphate Johnson and Adams[4] recommend that the precipitation be carried out in strongly acid solution (50 cc of concentrated hydrochloric acid in 350 cc) which is subsequently removed by evaporation to dryness. In this method the corrections necessary to apply are determined by a concurrent calibration of the method using pure dry sodium sulphate. "Incidentally

[1] Loc. cit.

[2] Bull. Soc. chim. Belg., **24**, 177 (1910).

[3] Jour. Biol. Chem., **1**, 147 (1906).

[4] Loc. cit.

it may be mentioned that the manipulation of the precipitate obtained from acid solutions is much easier and more rapid because of the coarseness of grain[1]...... One may evaporate to dryness immediately after precipitation and the precipitate being coarse-grained does not adhere at all to the vessel, is quickly filtered and easily washed and with less danger of loss in any of the operations."

The effect of the presence of hydrochloric acid on the crystal size has been studied both in the presence of barium ion and of sulphate ion in excess. Two sets of experiments were run with barium chloride and sulphuric acid and one

TABLE III

Solutions taken			Length of column of BaSO$_4$ cm		
H$_2$SO$_4$	BaCl$_2$	Conc. HCl	1	2	Mean
20 cc N/10	25 cc N/10	1 cc	1.12	1.04	1.08
25 cc N/10	20 cc N/10	1 cc	0.59	0.53	0.56
20 cc N/10	25 cc N/10	2 cc	0.74	0.73	0.74
25 cc N/10	20 cc N/10	2 cc	0.36	0.33	0.35
20 cc N/10	25 cc N/10	5 cc	0.57	0.46	0.52
25 cc N/10	20 cc N/10	5 cc	0.40	0.33	0.36
20 cc N/10	25 cc N/10	10 cc	0.58	0.49	0.53
25 cc N/10	20 cc N/10	10 cc	0.41	0.37	0.39
20 cc N/10	8 cc N	1 cc	4.62	4.80	4.71
8 cc N	20 cc N/10	1 cc	1.62	1.57	1.59
20 cc N/10	8 cc N	5 cc	1.45	1.40	1.43
8 cc N	20 cc N/10	5 cc	0.36	0.39	0.38
20 cc N/10	8 cc N	10 cc	1.09	0.99	1.04
8 cc N	20 cc N/10	10 cc	0.48	0.43	0.45
K$_2$SO$_4$	BaCl$_2$	Conc. HCl			
20 cc N/10	25 cc N/10	1 cc	1.09	—	1.09
25 cc N/10	20 cc N/10	1 cc	0.54	—	0.54
20 cc N/10	25 cc N/10	5 cc	0.40	—	0.40
25 cc N/10	20 cc N/10	5 cc	0.28	—	0.28
20 cc N/10	25 cc N/10	10 cc	0.33	—	0.33
25 cc N/10	20 cc N/10	10 cc	0.24	—	0.24

[1] Cf. Foulk: Jour. Am. Chem. Soc., **18**, 803 (1896).

with barium chloride and potassium sulphate, in the presence of varying amounts of hydrochloric acid. The acid was distributed equally between the two solutions before mixing. The method of procedure was identical with that given in the first part of this paper. Precipitations were made as previously described in a total volume of 100 cc. As before, the solution was allowed to stand for an hour before placing in the settling apparatus, and after the fifteen-minute interval the supernatant liquid was drawn off and centrifuged. Because of the larger particles obtained in the presence of hydrochloric acid, the centrifuging could be done immediately. The results are recorded in Table III.

Photomicrographs show that in the presence of small quantities of hydrochloric acid there are fewer skeleton crystals than in its absence. Needles, X's and H's predominate with lower concentrations of acid, and with higher concentrations these give place to large well formed rhombic crystals and plates.

Discussion of Results

The data contained in the above table together with the photomicrographs show two important facts: first, that barium sulphate is always more coarsely crystalline when precipitated in the presence of an appreciable amount of hydrochloric acid; and second, that with the same concentration of hydrochloric acid the physical character of the precipitate is better in the presence of sulphate ion in excess than with barium in excess. Assuming for the moment that hydrochloric acid has no solvent action on barium sulphate, the explanation of the second fact is quite evident. In the precipitation of sulphuric acid in the presence of hydrochloric acid with barium chloride in slight excess we should expect to get very finely divided particles because of the strong adsorption of both hydrogen ion and barium ion and the relatively weak adsorption of chlorine ion. The peptizing effect should be slightly less marked in the precipitation of potassium sulphate. In the precipitation of barium chloride in the presence of hydrochloric acid with sulphuric acid we should

get larger crystals since the adsorption of hydrogen ion is cut
down by the sulphate ions present. With a large excess of
hydrochloric acid and a small excess of sulphuric acid peptiza-
tion should result. For the same concentration of hydro-
chloric acid, therefore, larger crystals should be obtained
in the precipitation of barium ion with sulphate ion in ex-
cess, than in the reverse process. However, in the precipita-
tion in the presence of considerable hydrochloric acid the effects
of adsorption are of minor importance compared to the solvent
action of the acid itself. Because of this solvent action, large
crystals are always obtained in the presence of an excess of
hydrochloric acid.

The following is a summary of the results of this paper:

1. Barium sulphate shows a marked tendency to adsorb
many other substances.

2. Since any substance which is adsorbed by a second
will tend to peptize the latter, it follows that, other conditions
being the same, barium sulphate will come down most finely
divided when precipitated in the presence of those substances
for which it has the greatest specific adsorption.

3. In accordance with the general rule, barium sulphate
shows a marked adsorption for its own ions.

4. Positive colloidal solutions of barium sulphate, sta-
bilized by preferential adsorption of barium ion, have been
prepared by Kato and by Recoura.

5. A negative colloidal solution of barium sulphate, sta-
bilized by preferential adsorption of sulphate ion, has been
prepared.

6. Barium sulphate comes down very much finer when
precipitated with barium chloride in excess than with sul-
phuric acid in excess. Finer crystals are also obtained from
potassium sulphate solutions. The explanation of this is
as follows: Barium sulphate adsorbs its own ions strongly
and hydrogen ion is much more strongly adsorbed than most
cations. When sulphuric acid is precipitated by barium chlo-
ride the precipitate tends to come down in a finely divided
state because of the relatively strong adsorption of barium

ion and hydrogen ion. It would also come down very finely divided from sulphuric acid solution were it not that the strongly adsorbed hydrogen ion cuts down the adsorption of the sulphate ion. From potassium sulphate solution it comes down finely divided since potassium ion is not strongly adsorbed.

7. In the presence of hydrochloric acid barium sulphate comes down more finely divided with barium ion in excess than with sulphate ion in excess. In the first case, the cations hydrogen and barium are strongly adsorbed; in the second case, the presence of sulphate ion cuts down the adsorption of hydrogen ion.

8. Barium sulphate is always more coarsely crystalline when precipitated in the presence of an appreciable amount of hydrochloric acid. This is due to the solvent action of hydrochloric acid. In the presence of considerable excess of hydrochloric acid this solvent action is the predominant factor.

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THE POTENTIAL OF THE HYDROGEN ELECTRODE AT DIFFERENT PRESSURES

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In previous articles[1] it was pointed out that a thorough study of the relation between the hydrogen pressure and the electromotive force of the hydrogen electrode has been undertaken and in this note we shall point out some of the factors to be considered. We must study the effect of different hydrogen pressures at different temperatures, the rate of establishment of the gaseous and electrical equilibrium within the electrodes of different materials having different kinds of surfaces in order to study constant and especially *changing* solutions, and especially the problem of studying the mechanism of the establishment of the equilibrium between the molecules, atoms, and ions of hydrogen in and at the different kinds of electrodes. This last phase of the problem is also being studied by Prof. Edward Bennett and one of us in our investigations on the conductivities of solutions. Especial attention will be given to the well-known facts that between $100°$ and $180°$ hydrogen dissolves in palladium as hydrogen atoms[2] up to about 400 mm and above this pressure chiefly as H_2 to the extent of about 900 volumes. Platinum black[3] dissolves about 100 volumes of oxygen and 110 volumes of hydrogen up to 300 mm, and above this pressure up to 4–5 atmospheres the volume absorbed is practically constant for hydrogen but increases 8.5 volumes for oxygen. This last point may be significant in connection with the fact that the hydrogen-oxygen cell gives only 1.08 volts instead of 1.23. Experiments will be performed at 1–3000 mm at different temperatures to see whether at the critical pressures discussed above, 300 mm and 400 mm, there is any break in the e. m. f.-pressure-temperature relation which should involve (P-300)

[1] Jour. Phys. Chem., **19,** 663 (1916); Am. Chem. Jour., **46,** 585, 609.
[2] Hoitsema: Zeit. phys. Chem., **17,** 1 (1895).
[3] Ibid., **19,** 25 (1896).

and (P-400) instead of P.[1] This effect of pressure on the electromotive force must be considered all the more important because of such work as that of Harris[2] in which he found that in hydrogen gas the negative charge is associated with 1, 3, and 6 molecules of hydrogen and that the positive charge is associated with 9 molecules of hydrogen.

The importance of this study for making the barometric corrections when the worker does not employ a pressure-regulating device which we use, is obvious. The equilibrium apparently involves reactions which can be roughly sketched as $H_2 \text{ gas} \rightleftharpoons K \cdot H_2 \text{ elec.}$, $H_2 \text{ elec} \rightleftharpoons K \cdot \cdot \times 2H$ and $H + \oplus \rightleftharpoons K \cdot \cdot \cdot H$, whose velocities are not known. Maybe other forms of hydrogen such as H_3, etc., should also be considered. Since the work of Hoitsema,[3] and Langmuir show that at low pressures hydrogen exists largely in the atomic state in platinum and palladium black while at higher pressures it exists to a larger extent in the molecular state, and the same may occur in moist electrodes, it becomes simply an experimental question to determine whether these three constants change measurably with ordinary variation in atmospheric pressure, especially when the electromotive force can be measured to one-millionth volt. There are four sets of conditions which may be considered in developing equations: The first is the possibility that (a) the hydrogen absorbed by the electrode, $H_2 \text{ elec.}$, is directly proportional to the partial pressure of the hydrogen, $H_2 \text{ gas}$, that (b) the absorbed gas gives a constant concentration of hydrogen atoms, H, independent of the concentration of the absorbed hydrogen, just as the same volumes of different concentrations of an acid salt of a weak dibasic acid A_nH, give a constant concentration of hydrogen ions, and that (c) the hydrogen atoms in turn give a constant percentage of hydrogen ions, H. This assumption leads to

[1] Van't Hoff, Ibid., **5**, 328 (1890).

[2] Phil. Mag., **31**, 339 (1916).

[3] Zeit. phys. Chem., **17**, 1 (1895).

the equation $\overset{+}{H}$ = K, from which it follows that the e. m. f. would be independent of hydrogen pressure. As the experimental data are against this conclusion the above assumptions are incorrect. The second possibility differs from the first only in the assumption that the absorbed gas molecules, $H_{2\,elec.}$, then give a constant percentage of hydrogen atoms, H, just as aniline acetate is hydrolyzed to a constant percent independent of dilution. This assumption gives at once the equation $\overset{+}{H}$ = $KH_{2\,gas}$ and the equation $E = \dfrac{RT}{F} \log n \dfrac{H_{2\,gas}}{H'_{2\,gas}}$ would give the difference between two hydrogen electrodes saturated with the surrounding hydrogen gas at the pressures $H_{2\,gas}$ and $H'_{2\,gas}$. It is seen below that our experimental data at about atmospheric pressures do not harmonize with these equations and assumptions.

The third possibility differs from the second only in the assumption that in the moist electrodes the concentration of the absorbed molecular gas, $H_{2\,elec.}$, is proportional to the $1/2$ power of the hydrogen pressure, $H_{2\,gas}^{1/2}$, as has been found in other[1] similar cases of absorption. This assumption gives the equation $E = \dfrac{RT}{F} \log n \dfrac{H_{2\,gas}^{1/2}}{H'^{1/2}_{2\,gas}} = \dfrac{RT}{2F} \log n \dfrac{H_{2\,gas}}{H'_{2\,gas}}$.

The fourth case differs from the second in that it is assumed that the absorbed molecular gas gives hydrogen atoms in accordance with the equation $H_{2\,elec.} = K^{..} \times 2H$. If the equations be combined and written $\overset{+}{H} = K \sqrt{H_{2\,gas}}$, the thermodynamic equation becomes $E = \dfrac{RT}{nF} \log n \dfrac{\overset{+}{H}}{\overset{+}{H'}} = \dfrac{RT}{nF} \log n$

$\dfrac{K \sqrt{H_{2\,gas}}}{K \sqrt{H'_{2\,gas}}} = \dfrac{RT}{2F} \log n \dfrac{H_{2\,gas}}{H'_{2\,gas}}$ for the univalent hydrogen ion for expressing the change in E for a given electrode at two different pressures, $H_{2\,gas}$ and $H'_{2\,gas}$ in a given acid solution, *provided* K remains constant. The equations for this and the preceding case are therefore identical and the assumptions could

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[1] Hoitsema: Zeit. phys Chem., **17**, 1 (1895).

be differentiated by determining the relation of the amount of absorbed molecular gas, $H_{2\ elec}$ to the partial pressure of the hydrogen, $H_{2\ gas}$.

We have made 18 series of measurements at different pressures from 700 to 800 mm and find that the equation $E = \frac{RT}{2F} \log n\ H_2/H'_2$ holds very closely. This is in harmony with the one measurement by Ellis[1] and with the work of Lewis[2] and Rupert on the chlorine electrode. We shall not be satisfied, however, that this equation applies over a wide range of pressures, especially the lower ones, until we obtain further experimental evidence.

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[1] Jour. Am. Chem. Soc., **38**, 737 (1916).
[2] Ibid., **33**, 299 (1911).

NEW BOOKS

The Science of Musical Sounds. *By Dayton Clarence Miller. 22 × 16 cm; pp. viii + 286. New York: The Macmillan Company, 1916. Price: $2.50.—* The book is a development of a series of eight lectures on "Sound Analysis" delivered at the Lowell Institute in January and February, 1914. The titles of the eight lectures were: sound waves, simple harmonic motion, noise and tone; characteristics of tones; methods of recording and photographing sound waves; analysis and synthesis of harmonic curves; influence of horn and diaphragm on sound waves, correcting and interpreting sound analyses; tone qualities of musical instruments; physical characteristics of the vowels; synthetic vowels and words, relations of the art and science of music.

The chief scientific value of the book consists of course in the exposition of the quantitative details in regard to musical sounds, and the work of the author has been responsible for a surprisingly large part of what we know on this subject. The book has an added charm, however, because the author discusses incidentally a number of things which are of interest to the layman who may not care to follow the quantitative development of the subject very closely. The following extracts will give some idea of what is meant, pp. 21, 57, 175,179, 207, 242.

"Noise and tone are merely terms of contrast, in extreme cases clearly distinct, but in other instances blending; the difference between noise and tone is one of degree. A simple tone is absolutely simple mechanically; a musical tone is more or less complex, but the relations of the component tones, and of one musical sound to another, are appreciated by the ear; noise is a sound of too short duration or too complex in structure to be analyzed or understood by the ear. The distinction sometimes made, that noise is due to a non-periodic vibration, while tone is periodic, is not sufficient; analysis shows clearly that many so-called musical tones are non-periodic in the sense of the definition, and it is equally certain that noises are as periodic as are some tones. In some instances noises are due to a changing period, producing the effect of non-periodicity; but by far the greater number of noises which are continuous are merely complex and only apparently irregular, their analysis being more or less difficult. The ear, because of lack of training or from the absence of suitable standards for comparison or perhaps on account of fatigue, often fails to appreciate the character of sounds and, relaxing the attention, classifies them as noises."

"The determination of the acoustic properties of auditoriums is of the very greatest practical importance, and it is also one of the most elusive problems; the sounds which most interest us are of short duration and they leave no trace, and the conditions affecting the production, the transmission, and the perception of sounds are extremely complicated. The difficulties of the work are such as to discourage any but the most skillful and determined investigator. Indeed, the problem has been almost universally considered impossible of solution; and this opinion has been accepted with so much complacence, and even with satisfaction, that it still persists in spite of the fact that a scientific method of determining the acoustic properties of auditoriums has been developed by Professor Wallace C. Sabine of Harvard University. * * * * No auditorium,

large or small, and no music room, public or private, should be constructed which is not designed in accordance with these principles. Sabine's experiments have shown that the most common defect of auditoriums is due to reverberation, a confusion and diffusion of sound throughout the room which obscures portions of speech. There are other effects, due to echoes, interferences, and reflection in general, all of which have been considered. In many cases these troubles can be remedied, with more or less difficulty, in auditoriums already constructed; this is especially true in regard to reverberation, which is reduced by the proper use of thick absorbing felt placed on the side walls and ceiling."

"The sound-producing parts of a musical instrument, in general, perform two distinct functions. Certain parts are designed for the production of musical vibrations. The vibrations in their original form may be almost inaudible, though vigorous, because they do not set up waves in the air, as is illustrated by the vibrations of the string of a violin without the body of the instrument; or the vibrations may produce a very undesirable tone quality because they are not properly controlled, as in the case of the reed of a clarinet without the body tube. Other parts of the instrument receive these vibrations, and by operation on a larger quantity of air and by selective control, cause the instrument to send out into the air the sounds which we ordinarily hear. These parts, which may be referred to as *generator* and *resonator*, are illustrated by the following combinations: a tuning fork generator and its box resonator; the strings and soundboard of a piano; the reed and body tube of a clarinet; the mouth and body tube of an organ pipe; the vocal cords and mouth cavities of the voice. In the piano the soundboard acts as a universal resonator for all the tones emitted by the instrument; in the organ each pipe constitutes its own separate resonator; in the flute the body tube is adjusted to various different conditions by means of holes and keys, each condition serving for several tones.

"The resonator cannot give out any tones except those received from the generator, and it may not give out all of these. The generator must therefore be capable of producing components which we wish to hear, and these must in turn be emitted in the desired proportion be the resonator. If the generator produces partial tones which are undesirable, the resonator should be designed so that it will not reproduce them; if the generator produces tones which are of musical value but which the resonator does not produce, we do not hear them, and it is as though they were not produced at all. It follows that we can hear from a given instrument nothing except what is produced by the generator, and further we can hear nothing except what is also reproduced by the resonator; hence it may be that the most important part of an instrument is its resonator. The quality of any tone depends largely upon the kind and degree of sympathy, or resonance, which exists between the generator and the resonator."

"Both the tones generated by a musical instrument and those reproduced, as well as those absorbed or damped, depend in a considerable degree upon the material of which the various parts of the instrument are constructed While this fact is well known and commonly made use of in connection with certain classes of instruments, its truthfulness is often denied by the devotees of other instruments. The question of the influence of the material of which the body tube of a flute is made has not been settled after more than seventy years of widespread discussion. How does the tone from a gold or silver flute differ from that

of a wooden flute? It was this specific question that suggested the investigations which, having passed much beyond the original inquiry, have furnished the material upon which this course of lectures is based.

"The following experiments, suggested by those of Schafhäutl, indicate the great changes in the tone of an organ pipe which may be produced by effects passing through the walls. Three organ pipes are provided. The first pipe, of the ordinary type used in physical experiments, is made of wood and sounds the tone $G_1 = 192$. Two pipes having exactly the same internal dimensions as the wooden one are made of sheet zinc about 0.5 millimeter thick. One of the zinc pipes has been placed inside a zinc casing to form a double-walled pipe, with spaces two centimeters wide between the walls; the outer wall is attached to the inner one only at the extreme bottom on three sides, and just above the upper lip-plate on the front side. These two pipes have exactly the same pitch, giving a tone a little flatter than F_2, which is more than two musical semitones lower than that of the wooden pipe of the same dimensions.

"Using the single-walled zinc pipe one can produce the remarkable effect of choking the pipe till it actually squeals. When the pipe is blown in the ordinary manner, its sound has the usual tone quality. If the pipe is firmly grasped in both hands just above the mouth, it speaks a mixture of three clearly distinguished inharmonic partial tones, the ratios of which are approximately $1 : 2.06 : 2.66$. The resulting unmusical sound is so unexpected that it is almost startling, the tone quality having changed from that of a flute to that of a tin horn.

"Experiments with the double-walled pipe are perhaps more convincing. While the pipe is sounding continuously, the space between the walls is filled slowly with water at room temperature. The pipe, with the dimensions of a wooden pipe giving the tone G_2, when empty, has the pitch F_2, and when the walls are filled with water the pitch is E_2; during the filling the pitch varies more than a semitone, first rising then falling. While the space is filling, the tone quality changes conspicuously thirty or forty times.

"After the demonstration of these effects, one will surely admit that the quality of a wind-instrument may be affected by the material of its body tube to the comparatively small extent claimed by the player. The flute is perhaps especially susceptible to this influence because its metal tube is usually only 0.3 millimeter thick. It is conceivable that the presence or absence of a ferrule or of a support for a key might cause the appearance or disappearance of a partial tone, or put a harmonic partial slightly out of tune.

"The traditional influence of different metals on the flute tone are consistent with the experimental results obtained from the organ pipe. Brass and German silver are usually hard, stiff, and thick, and have but little influence upon the air column, and the tone is aid to be hard and trumpet-like. Silver is denser and softer, and adds to the mellowness of the tone. The much greater softness and density of gold adds still more to the soft massiveness of the walls, giving an effect like the organ pipe surrounded with water. Elaborate analyses of the tones from flutes of wood, glass, silver, and gold prove that the tone from the gold flute is mellower and richer, having a longer and louder series of partials, than flutes of other materials.

"Mere massiveness of the walls does not fulfill the desired condition; a heavy tube, obtained from thick walls of brass, has such increased rigidity as to pro-

duce an undesirable result; the walls must be thin, soft, and flexible, and must
be made massive by increasing the density of the material. The gold flute
tube and the organ pipe surrounded with water, are, no doubt, similar to the
long strings of the pianoforte, which have a rich quality; these strings are wound
or loaded, making them massive, while the flexibility or "softness" is unimpaired.
The organ pipe partly filled with water is like a string unequally loaded, its partials
are out of tune and produce a grotesque tone. A flute tube having no tone holes
or keys is influenced by the manner of holding; certain overtones are some-
times difficult to produce until the points of support of the tube in the hands
have been altered."

"The piano is perhaps the most expressive instrument, and therefore, the
most musical, upon which one person can play, and hence it is rightly the most
popular instrument. The piano can produce wonderful varieties of tone color
in chords and groups of notes, and its music is full, rich, and varied. The sounds
from any one key are also susceptible of much variation through the nature of
the stroke on the key. So skillful does the accomplished performer become
in producing variety of tone quality in piano music, which expresses his musical
moods, that it is often said that something of the personality of the player is
transmitted by the 'touch' to the tone produced, something which is quite inde-
pendent of the loudness of the tone. It is also claimed that a variety of tone
qualities may be obtained from one key, by a variation in the artistic or emo-
tional touch of the finger upon the key, even when the different touches all pro-
duce sounds of the same loudness. This opinion is almost universal among
artistic musicians, and doubtless honestly so. These musicians do in truth
produce marvelous tone qualities under the direction of their artistic emotions,
but they are primarily conscious of their personal feelings and efforts, and seldom
analyze thoroughly the principles of physics involved in the complicated me-
chanical operations of tone production in the piano. Having investigated this
question with ample facilities, we are compelled by the definite results to say
that, if tones of the same loudness are produced by striking a single key of a
piano with a variety of touches, the tones are always and necessarily of identical
quality; or, in other words, a variation of artistic touch cannot produce a varia-
tion in tone quality from one key, if the resulting tones are all of the same loud-
ness. From this principle it follows that any tone quality which can be produced
by hand playing can be reproduced identically by machine playing, it being
necessary only that the various keys be struck automatically so as to produce
the same loudness as was obtained by the hand, and be struck in the same time
relation to one another. There are factors involved in the time relations of be-
ginning the several tones of a chord or combination, which are often taken into
account; a brief notice of the nature of piano tone will enable us to establish this
conclusion.

"Whatever complex tone may be generated by the hammer blow, the quality
of tone that enters into combination with that from other strings is dependent
upon the parts of the tones from the several strings being simultaneously coex-
istent. The quality of tone obtained from a piano when a melody note is struck
is dependent upon the mass of other tones then existing from other keys previously
struck and sustained, and it depends upon the length of time each of these tones
has been sounding. It is evident that not only does a piano give great variety of

tone by various degrees of hammer blow, but there is possible an almost infinite variety of tone quality in combinations of notes struck at intervals of a few hundredths of a second. It is believed that the artistic touch consists in slight variations in the time of striking the different keys, as well as in the strength of the blow, and that tone quality is determined by purely physical and mechanical considerations."

"Peculiarities of individual voices are probably due to the presence or absence of particular overtones in the larynx sound, according to incidental or accidental conditions. A low voice of a man has a large number of partials not essential to the vowel, which, so to speak, overload the characteristic tones; these partials may make the voice louder, but the detract from clearness of enunciation. A child's voice, on the contrary, produces only the higher tones, and but few besides those necessary for the vowel; the enunciation is, therefore, especially clear, clean-cut, and distinct. One is conscious of the greater clearness of enunciation of a child's voice when listening to a conversation in a foreign language which is understood with difficulty.

"The process of singing a vowel is probably as follows: The jaws, tongue, and lips, trained by lifelong practice in speaking and singing, are set in the definite position for the vowel, and the mouth is thus tuned unconsciously to the tones characteristic of that vowel. At the same time the vocal cords of the larynx are brought to the tension giving the desired pitch, automatically if one is trained to sing in tune, but usually as the result of trial. When the air from the lungs now passes through the larynx, a composite tone is generated, consisting of a fundamental of the given pitch accompanied by a long series, perhaps twenty in number, of partials, usually of a low intensity. The particular partials in this series which are most nearly in unison with the vibrations proper to the air in the mouth cavity, are greatly strengthened by resonance, and the resultant effect is the sound which the ear identifies as the specified vowel sung at the designated pitch."

Where so much has been given, it is perhaps unreasonable to ask for more; but the reviewer would have welcomed a few lines about the physical differences between bell metal and the other bronzes or lead.   *Wilder D. Bancroft*

A Chemical Sign of Life. *By Shiro Tashiro. 19 × 13 cm; pp. ix + 142. Chicago: The University of Chicago Press, 1917. Price: $1.00 net.*—The author points out, p. 4, that "there are two signs, or tests, which all living things show and which are an index of life. One of these is an electrical disturbance. This was discovered a very long time—a hundred years—ago, and its discovery was the basis of the development of knowledge of electricity. The other is a chemical sign, which has just been discovered and which will be discussed in this book. The electrical sign of life was discovered by Galvani when he found that animal tissues are a source of electricity. He discovered animal electricity. It is now certain that whenever the response to a stimulus takes place in animals or plants— the response which is the sign of life—an electrical change accompanies it. By placing a galvanometer on the animal or plant we can study this electrical response. Life and electricity are thus shown to be related. Electricity and psychism have something in common, although just what the connection is cannot at present be said. The English physiologist Waller has recently intro-

duced as a measure of life a particular kind of electrical response which he has discovered and which he calls the "blaze" current, because it is as if the electrical display suddenly blazed up when the living matter was disturbed; this he calls an electrical sign of life. By it he can tell whether a dry seed is alive or not without putting it in the ground and letting it sprout. It is very hard to know whether this electrical disturbance which living things show is due to physical or to chemical changes in their substances.

"It is therefore a matter of very great interest that I have recently found that there is always and everywhere an accompanying chemical change of a particular kind which is as sure a sign of life and as invariable an accompaniment of the vital reaction as the electrical change. This chemical sign is the sudden outburst of carbon dioxide which all living things show—plants as well as animals, dry seeds as well as the nerve tissues of the highest mammals—when they are stimulated in any way. The instrument which I have made to detect this carbon dioxide I have called a 'biometer' because, as will be appreciated from this short discussion, it is an apparatus for measuring or detecting the amount of life possessed by different things. I shall show in the following pages that the increment of carbon dioxide produced by living things when they are irritated, or stimulated in any way, is a sure measure of the amount of life they have; and we may hope that it is to be an indirect measure of the amount of psychism they possess, although of course we cannot be sure of this as yet. It will be noticed that it is not the absolute amount of carbon dioxide which is the measure of life, but the increase above the usual production which occurs when a definite amount of stimulus is applied to the living things, which is the real measure of life. Anesthetized or sick things do not show the normal increase; those abounding in life show a remarkable increase."

On p. 102 the author says: "The chemical sign of life which we now propose for acceptance is in many ways more fundamental than the electrical   It is probable, as Waller suggested, that the chemical changes underlie and produce the electrical, and they produce the functional changes, such as the movements which follow the excitation. In the chemical changes, then, we seem to be dealing with something more fundamental than when dealing with the electrical, although, if we admit that all processes of oxidation are in reality electrical, this distinction cannot be sustained. Wherever Waller has been able to show the electrical sign of life, we can show the chemical sign, and we can show life at some points where he could not, as in the case of the sea algae. These, under our method, respond in the same manner as do all other forms of living matter. Moreover, we can use this method where it is impossible to use the electrical; for example, in very minute forms of living things, like eggs of small size, bacteria, or infusoria. Our method can make it clear that they are alive and breathing and responding to changes in their environment like every other living thing. It appears, then, that this sign of life has also certain virtues of its own, although it is not so striking and elegant as the method of Waller. It is also not so easy, perhaps, for the ordinary man to set up and work this apparatus as a galvanometer But what it lacks in ease it makes up in precision, in the quantitative nature of its results, and, above all, in its fundamental character. By it we get as near as we have yet got to life itself.

"In still another way the results which are recorded here are of a most funda-

mental character, for one of the most interesting problems of general physiology has been to determine what is the nature of the irritable response which living matter shows. It is this, the problem of problems, which we wish to have solved. Is that process physical or chemical? Is it simply an alteration of permeability of membranes, as some have supposed, or is it in reality in the nature of an explosion? Is the living thing essentially a bag of jelly with a wonderful membrane about it, that membrane being so wonderful that all the phenomena of life are to be ascribed to its changes in state? For this is the view which some maintain. They lead us to the holy of holies of cells and tell us to behold a membrane! Is life nothing more than a membrane? What kind of a subterfuge is this which we encounter? All the riddles of life are but the peculiar properties of a membrane! Upon this membrane, as upon a magic carpet of Arabia, we are invited to mount and travel over that unexplored country whose mountain peaks shine in the distance. Are we, then, beings of but two dimensions, nothing but membranes, of which the magic proportions mock us derisively, since we can never hope to seize that which has but two dimensions? That such a view resembles the membrane it has conjured up, in that it is surface without depth, is self-evident. In no such simple and naive a manner can the unknowns in the equation of life be determined. For we have found that everywhere, paralleling the irritability changes in a perfect degree, as far as we have been able to determine, go the chemical changes. Carbon dioxide, that very simple substance, the last term in the catabolism of living matter, rises and falls with irritability. Function without chemical change has been found nowhere. Respiration, or at least this phase of respiration, and irritability are in some way bound up together, and we may now very briefly ask ourselves how they may be related."

"This book contains somewhat in detail all the essential facts which the author with his students has discovered from studies of the chemical changes in nerves accompanying functional change. In the presentation of this work, however, many important references and discussions have been omitted in order that the reader may not lose the main trend of the argument. The facts themselves are nevertheless given in the form of accurate numerical data so that the book may be useful also to the specialist whose interest lies more directly in the general physiology of the nervous system." ,

The chapters are entitled: irritability as a sign of life; chemical signs of irritability in the nerve fiber; excitation and conduction; chemical signs of life; conclusions. *Wilder D. Bancroft*

MOLECULAR ATTRACTION. XIV. SPECIFIC HEATS OF THE ELEMENTS AND SOME ENERGY CHANGES

BY J. E. MILLS

In work upon molecular forces and the related energy changes it seemed advisable to collect and examine more fully than has yet been done the data upon the specific heats, heats of fusion, heats of vaporization, and heats of transformation from one allotropic form into another, of the elements. The results of this work are here published in part. The references and the original data are not here given. This omission is regrettable but necessary. If work upon the elements alone is considered some 500 references to the work of about 300 men have been consulted. Many of these workers have made extensive investigations. Merely to give the references and briefest necessary critical comment would greatly exceed the limits of a journal article. Much effort has been spent to make the collection of the data as complete and as accurate as possible and it is nearly ready for publication should its publication in some form later seem to be desirable.

In reconciling, smoothing, and digesting the data in order to obtain the results here given I have not been biased by any preconceived theory. I have tried to follow the most accurate measurements that had been made and, therefore, have had to rely upon my own judgment as to the probable accuracy of the results at hand. In many cases more accurate data are greatly to be desired.

No data could be found for columbium,, dysprosium, erbium, europium, fluorine, gadolinium, holmium, lutecium, neodymium, praeseodymium, radium, samarium, scandium, terbium, thulium, ytterbium and yttrium.

For the elements given in Table 1 data were not sufficient to allow the drawing of reasonably good smoothed specific heat curves and data that are at hand are, therefore, published here.

TABLE 1—SPECIFIC HEATS, ETC.

	Temperature	Per gram		Temperature	Per gram
Barium]			Richards and Jackson	—188, 20	0.058
Mendeléeff					
Nordmeyer and Ber-			*Krypton*		
nouilli	—185, 20 20K, 80K	0.05	Ramsay　γ	19°	1.689
Dewar　(Impure)		0.0681 0.0350	Rudorf　C L$_v$	121.4K	27.55
Cerium			*Lanthanum*		
Mendeléeff	0, 100	0.05	Hillebrand	0, 100	0.4485
Hillebrand	20, 100	0.04479	Dewar	20K, 80K	0.322
Hirsch	20K, 80K	0.05112			
Dewar		0.0330	*Neon*		
Gallium			Ramsay　γ	19	1.642
Berthelot　Liquid	12, 23 13, 112	0.079 0.0802			
L$_f$	13.5	19.11	*Niton*		
			De Forcrand　C L$_v$	211K	19.15
Germanium			Ramsay and Gray C L$_v$	211K	18.59
Nilson and Pettersson	0, 100 0, 211 0, 301.5 0, 440	0.0737 0.0773 0.0768 0.0757	Chaumat　L$_v$	211K	18.67
			Rudorf　C L$_v$	211K	23.59
Indium			C L$_v$	211K	18.62
Bunsen	0, 100	0.05695			

TABLE I—(*Continued*)

	Temperature	Per gram		Temperature	Per gram
Niobium			*Vanadium*		
Muthmann, Weiss and Riedelbauch	17.3, 98.2	0.0617	Setterberger	15, 100	0.1259
Abegg's Handbuch, etc.	21, 100	0.071	Mache	0, 100	0.1153
Osmium			Muthmann, Weiss and Riedelbauch	17, 98.5	0.1240
Regnault	19, 98	0.03113	*Xenon*		
Dewar	20K, 80K	0.0078	Ramsay γ	19	1.666
Rhodium			Rudorf $C\ L_\sigma$	163.7K	23.80
Regnault	10, 97	0.05803	*Zirconium*		
Dewar	20K, 80K	0.0134	Mixter and Dana	0, 99.7	{ 0.0667 / 0.0735
Ruthenium			Wedekind and Lewis	0, 100	{ 0.6083 / 0.0656
Bunsen	0, 100	0.0611	Weiss and Neumann	19.6, 98.6	0.0804
Dewar	20K, 80K	0.0109	Dewar	20K, 80K	0.0262
Strontium					
Glascock		0.0742			
Dewar (Impure)	20K, 80K	0.0550			
Thorium					
Nilson	0, 100	0.02787			
Dewar	20K, 80K	0.0197			
Uranium					
Regnault	11, 98	0.06190			
Zimmerman	0, 99	0.02765			
Blümcke	0, 99	0.0280			
Dewar	20K, 80K	0.0138			

In Table 1 and throughout this paper, σ, σ_p, σ_v denote specific heat of solid (or liquid), specific heat at constant pressure, and specific heat at constant volume, respectively. γ denotes the ratio of the specific heat of a gas at constant pressure to the specific heat of the gas at constant volume. L_f denotes heat of fusion, L_v heat of vaporization, L_s heat of sublimation, and L_t heat of transformation. C before these symbols means that the result was not a direct measurement. Since the calculations are quite often based on thermodynamical formulas the results may be quite as accurate as more direct measurements. K denotes absolute temperature. Other temperatures are centigrade.

In Table 1 when two temperatures are named the value of the specific heat given is for the mean specific heat between the temperatures given. When only one temperature is given the value is supposed to be the value of the measurement at the temperature named. When no temperature is given the value is probably a mean value at or near room temperature.

Table 2 contains, the smoothed specific heats per gram, and per gram molecular weight, of the remaining elements, except for the gases which are discussed later. The "average" value given at the bottom of the table is the total heat in the liquid at its melting point divided by the absolute temperature of the melting point. A line across a column indicates that the specific heat curve becomes linear to the next line. (The specific heats above where the lines were drawn in the manuscript have been placed in italics and this will serve the purpose intended.) *Careful attention must be paid to the notes immediately following the table since the values of the specific heats given in the table differ greatly in their probable accuracy.* Also transformation points and accompanying heat changes are given in the notes. No attempt is made to discuss all of the data in the notes. The notes are numbered to correspond with the number of the element in Table 2. Parentheses around a value indicate an extrapolated result. Modern determinations would seem to prove conclusively that the specific heat of all elements (and compounds) approaches zero at the absolute zero.

TABLE 2—SPECIFIC HEAT

Temperature	1. Aluminum Gram	1. Aluminum Gram-atom	2. Antimony Gram	2. Antimony Gram-atom	4. Arsenic Gram	4. Arsenic Gram-atom	5 Bismuth Gram	5 Bismuth Gram-atom	6. Boron (cryst.) Gram	6. Boron (cryst.) Gram-atom
50° K	0 035	0 94	0.0240	2.88	0.0258	1.93	0.0218	4.54	0.0212	0.23
100 K	0 111	3.01	0 0390	4 69	0.0494	3.70	0.0254	5.28	0.0375	0.41
150 K	0.160	4.34	0.0455	5 47	0.0645	4 83	0.0282	5.87	0.0830	0.91
200 K	0.188	5 10	0.0472	5.67	0.0716	5.37	0.0296	6.16	0.145	1.59
250 K	0.204	5 52	0 0482	5 79	0.0772	5.79	0.0300	6.24	0.197	2.17
0° C	0.208	5 64	0 0486	5 84	0 0794	5.95	0.0301	6 26	0.217	2.39
50	0.217	5 88	0 0495	5.95	0 0833	6.25	0 0304	6 32	0.255	2 80
100	0.224	6.07	0 0505	6.07			0 0307	6 38	0.290	3.19
200	0.233	6.32	0.0524	6.30			0.0312	6.49	0 349	3.84
300	0.243	6.60	0.0544	6.54						
400	0.256	6.94	0.0563	6.77						
500	0.274	7 42	0.0583	7.01						
600	0.300	8.12	0.0602	7.24						
700										
800										
900										
1000										
Melting point	658°		630°		500°		271°			
Solid	0.319	8 64	0.0608	7 31	—	—	0 0316	6.57	—	—
Liquid	{ 0.391 0.308	8.35	—	—	—	—	0.0363	7 55	—	—
Average	0.304	8.23	0 0938	11 27	—	—	0.0504	10.49	—	—

TABLE 2—SPECIFIC HEAT (Continued)

Temperature	7. Bromine		8. Cadmium		9. Caesium		10. Calcium		11. Carbon graphite	
	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom
50° K	0.045	3.60	0.0308	3.46	0.0513	6.82	0.071	2.85	0.0093	0.11
100 K	0.061	4.88	0.0469	5.27	0.0515	6.84	0.122	4.89	0.0335	0.42
150 K	0.075	6.00	0.0514	5.78	0.0517	6.86	0.138	5.53	0.0663	0.80
200 K	0.088	7.04	0.0533	5.99	0.0519	6.89	0.144	5.77	0.1024	1.23
250 K	0.102	8.16	0.0544	6.12	0.0521	6.92	0.149	5.97	0.1389	1.67
0° C			0.0548	6.16	0.0522	6.93	0.152	6.09	0.156	1.87
50			0.0560	6.29			0.157	6.29	0.195	2.34
100			0.0572	6.43			0.161	6.45	0.233	2.80
200			0.0595	6.69			0.170	6.81	0.298	3.58
300			0.0618	6.95			0.179	7.17	0.348	4.18
400							0.202	8.09	0.386	4.63
500									0.415	4.98
600									0.436	5.23
700									0.450	5.40
800									0.459	5.51
900									0.405	5.58
1000									0.467	5.60
Melting point	265.7° K		320.9°		28.45°		803°		Volatilizes 3600°	
Solid	0.106	8.48	0.0622	6.99	0.0600	7.97	—	—	0.817	9.80
Liquid	0.107	8.56	—	—	0.0595	7.90	—	—	—	—
Average	0.124	9.88	0.0744	8.36	0.0628	8.34	—	—	—	—

TABLE 2—SPECIFIC HEAT (*Continued*)

Temperature	11. Carbon diamond		12. Chlorine		13. Chromium		14. Cobalt		15. Copper	
	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom
50° K	0.0008	0.01	0.097	3.45	0.014	0.74	0.021	1.24	0.0208	1.32
100 K	0.0070	0.08	0.135	4.79	0.046	2.39	0.055	3.24	0.0620	3.94
150 K	0.0227	0.27	0.159	5.64	0.072	3.74	0.073	4.31	0.0794	5.05
			Liquid	Liquid						
200 K	0.0495	0.59	0.216	7.66	0.089	4.63	0.087	5.13	0.0854	5.43
250 K	0.0847	1.02	0.223	7.91	0.100	5.20	0.096	5.66	0.0895	5.69
0° C	0.103	1.24	0.226	8.01	0.104	5.41	0.099	5.84	0.0909	5.78
50	0.146	1.75			0.109	5.66	0.103	6.08	0.0931	5.92
100	0.189	2.27			0.113	5.88	0.106	6.25	0.0952	6.05
200	0.268	3.22			0.118	6.14	0.113	6.67	0.0985	6.26
300	0.330	3.96			0.123	6.40	0.121	7.14	0.1018	6.47
400	0.370	4.44			0.128	6.66	0.132 (508°)	7.79 (508°)	0.1050	6.68
500	0.401	4.81			0.134	6.97	0.145 (508°)	8.55 (508°)	0.1083	6.88
600	0.426	5.11			0.150	7.80	0.125	7.37	0.1115	7.09
700	0.441	5.29					0.136	8.02	0.1148	7.29
800	0.449	5.39					0.148	8.73	0.1180	7.50
900	0.454	5.45					0.160	9.44	0.1213	7.70
1000	0.460	5.52					0.172	10.15	0.1245	7.91
1112							0.184	10.86		
1200							0.270	15.93		
Melting point			169.5° K		1550°		1478°		1083°	
Solid			0.170	6.03			0.172	10.15	0.1272	8.08
Liquid			0.212	7.52			0.172	10.15	0.132	8.37
Average			0.249	8.84						

TABLE 2—SPECIFIC HEAT (*Continued*)

Temperature	16. Glucinum Gram	16. Glucinum Gram-atom	17. Gold Gram	17. Gold Gram-atom	20. Iodine Gram	20. Iodine Gram-atom	21. Iridium Gram	21. Iridium Gram-atom	22. Iron Gram	22. Iron Gram-atom
50° K	0.0137	0.12	0.0160	3.16	0.0373	4.74	0.0099	1.91	0.0175	0.98
100 K	—	—	0.0260	5.12	0.0430	5.46	0.0216	4.17	0.0510	2.85
150 K	—	—	0.0277	5.46	0.0454	5.77	0.0266	5.13	0.0770	4.30
200 K	—	—	0.0288	5.68	0.0478	6.07	0.0290	5.60	0.0938	5.24
250 K	—	—	0.0298	5.88	0.0502	6.38	0.0306	5.91	0.1018	5.68
0° C	0.376	3.42	0.03020	5.96	0.0514	6.53	0.0312	6.02	0.104	5.81
50	0.425	3.87	0.03042	6.00	0.0538	6.84	0.0322	6.21	0.1095	6.11
100	0.470	4.28	0.03065	6.05	0.0563	7.15	0.0330	6.37	0.115	6.42
200	0.542	4.93	0.03110	6.13					0.126	7.03
300	0.591	5.38	0.03154	6.22					0.137	7.65
400	0.617	5.61	0.03199	6.31					0.148	8.26
500	0.621	5.65	0.03243	6.40					0.159	8.88
600			0.03288	6.48					0.170	9.49
700			0.03332	6.57					0.181	10.11
800			0.03377	6.66					0.192	10.72
900			0.03421	6.75					0.203	11.34
1000			0.03466	6.83					0.167	9.33
1400										
Melting point	Under 1000°		1062.4°		113.5°		2290°		1530°	
Solid	—	—	0.0349	6.88	0.0570	7.24	0.0485	9.36	0.167	9.33
Liquid	—	—	—	—	0.108	13.73	—	—	—	—
Average	—	—	0.0431	8.50	0.0758	9.60	—	—	0.189	10.55

TABLE 2—SPECIFIC HEAT (*Continued*)

Temperature	23 Lead		24 Lithium		25 Magnesium		26 Manganese		27 Mercury	
	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom
50° K	0.0251	5.20	0.193	1.34	0.069	1.68	0.023	1.26	0.02487	4.99
100 K	0.0283	5.86	0.440	3.05	0.169	4.11	0.064	3.52	0.02891	5.80
150 K	0.0289	5.98	0.547	3.80	0.202	4.91	0.085	4.67	0.03071	6.16
200 K	0.0294	6.10	0.650	4.51	0.219	5.33	0.097	5 33	0.03230	6.48
									Liquid	Liquid
250 K	0.0300	6.22	0.753	5.23	0.232	5.64	0.104	5.71	0.03374	6.77
0° C	0.0303	6.28	0 800	5.55	0.238	5.79	0 107	5.88	0.03350	6.72
50	0.0309	6.39	0.903	6.27	0.246	5.98	0 111	6 10	0.03307	6.63
100	0.0314	6.50	1.005	6.97	0.253	6.15	0 114	6 26	0.03289	6.60
200	0.0325	6.73			0 263	6.39	0 121	6.65	0.03292	6.60
300	0.0336	6.96			0.273	6.64	0.131	7.20	0.03336	6.69
400					0.282	6.86	0.145	7.96		
500					0.288	7.00	0.165	9.06		
600										
700										
800										
900										
1000										
356.95										
Melting point	327.4°		180°		650°		1260°		(0.03368) 234.15° K	(6.76)
Solid	0.0339	7.02	1.169	8 11	(0.298)	(7 25)	—	—	0.03320	6.66
Liquid	0.0406	8.41	—	—	0 374	9.09	—	—	0.03390	6.80
Average	0.0383	7.93	0.719	4.99	0.320	7.78	—	—	0.03858	7.74

TABLE 2—SPECIFIC HEAT (*Continued*)

Temperature	28. Molybdenum		29. Nickel		32. Palladium		33. Phosphorus Red		33. Phosphorus Yellow	
	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom
50° K	0.0141	1.35	0.021	1.23	0.019	2.03	0.042	1.30	0.074	2.30
100 K	0.0304	2.92	0.054	3.17	0.043	4.59	0.082	2.55	0.108	3.35
150 K	0.0461	4.43	0.075	4.40	0.050	5.33	0.114	3.54	0.130	4.04
200 K	0.0575	5.52	0.089	5.22	0.054	5.76	0.135	4.19	0.152	4.72
250 K	0.0659	6.33	0.100	5.87	0.057	6.08	0.152	4.72	0.169	5.25
0° C	0.0683	6.56	0.103	6.04	0.0582	6.21	0.160	4.97	0.175	5.43
50	0.0722	6.93	0.108	6.33			0.175	5.43		
100	0.0727	6.98	0.113	6.61			0.189	5.87		
200	0.0737	7.08	0.123	7.19			0.204	6.33		
300	0.0747	7.17	0.133	7.76			0.205	6.36		
400	0.0757	7.27	0.126	7.38						
500			0.131	7.68						
600			0.136	7.98						
700			0.141	8.27						
800			0.146	8.57						
900			0.152	8.87						
1000			0.157	9.17						
370			0.139	8.16						
Melting point	2535°		1452° { 0.124 }	7.28	1549.2°		—	—	44.0°	
Solid					0.0835	8.91			0.186	5.77
Liquid					—	—			0.204	6.35
Average					0.0862	9.20			0.155	4.80

TABLE 2—SPECIFIC HEAT (*Continued*)

Temperature	34. Platinum — Gram	34. Platinum — Gram-atom	35. Potassium — Gram	35. Potassium — Gram-atom	36. Rubidium — Gram	36. Rubidium — Gram-atom	37. Selenium — Gram	37. Selenium — Gram-atom	38. Silicon — Gram	38. Silicon — Gram-atom
50° K	0.0135	2.63	0.1280	5.00	0.0711	6.05	0.0361	2.86	0.016	0.45
100 K	0.0272	5.31	0.1517	5.93	—	—	0.0525	4.16	0.063	1.78
150 K	0.0286	5.58	0.1580	6.18	—	—	0.0630	4.99	0.099	2.80
200 K	0.0296	5.78	0.1620	6.33	—	—	0.0703	5.57	0.128	3.62
250 K	0.0305	5.95	0.1680	6.57	—	—	0.0763	6.04	0.151	4.27
0° C	0.0310	6.05	0.1729	6.76	0.0802	6.86	0.0790	6.26	0.160	4.53
50	0.0318	6.21	0.1875	7.33			0.0850	6.73	0.177	5.01
100	0.0323	6.30					0.0910	7.21	0.190	5.38
200	0.0332	6.48					0.1030	8.16	150 = 0.199	5.63
300	0.0340	6.64							0.201	5.69
400	0.0348	6.79							250 = 0.202	5.72
500	0.03560	6.95								
600										
700	0.03685	7.19								
800										
900	0.03799	7.42								
1000										
1100	0.03901	7.62								
1300	0.04003	7.81								
1500	0.04073	7.95								
Melting point	1755°		63.5°		39.0°		217°		1414°	
Solid	(0.0418)	(8.17)	0.1914	7.48	0.0919	7.85	(0.1050)	(8.32)	—	—
Liquid	—	—	0.1844	7.21	0.0911	7.78	—	—	—	—
Average	0.0490	9.56	0.195	7.62	0.0934	7.98				

TABLE 2—SPECIFIC HEAT (Continued)

Temperature	39. Silver		40. Sodium		41. Sulphur				42. Tantalum	
					Rhombic		Monoclinic			
	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom
50° K	0.0253	2.73	0.152	3.50	0.055	1.76	0.059	1.89	0.0150	2.72
100 K	0.0441	4.76	0.229	5.27	0.096	3.08	0.100	3.21	0.0250	4.54
150 K	0.0507	5.47	0.256	5.89	0.122	3.92	0.131	4.20	0.0284	5.15
200 K	0.0535	5.77	0.267	6.14	0.142	4.55	0.155	4.97	0.0305	5.54
250 K	0.0552	5.95	0.278	6.39	0.158	5.08	0.170	5.45	0.0324	5.88
0° C	0.0556	6.00	0.284	6.53	0.166	5.32	0.174	5.58	0.0331	6.01
50	0.0560	6.04	0.295	6.78	0.176	5.65	0.185	5.93	0.0344	6.24
100	0.0564	6.08	60° = 0.297	6.83	0.183	5.87	0.196	6.29	0.0358	6.50
200	0.0571	6.16	70° = 0.303	6.97						
300	0.0579	6.25	80° = 0.309	7.12						
400	0.0592	6.39	90° = 0.325	7.47						
500	0.0621	6.70								
600	0.0655	7.07								
700										
800										
900										
1000										
Melting point	960.9°		97.9°		110.2°		114.6°		2850°	
Solid	(0.0730)	(7.88)	0.329	7.57	0.185	5.93	0.199	6.38	—	—
Liquid	0.0748	8.07	0.323	7.43	0.228	7.31	0.228	7.31	—	—
Average	0.0778	8.39	0.312	7.17	0.164	5.30	0.164	5.28	—	—

TABLE 2—SPECIFIC HEAT (*Continued*)

Temperature	43. Tellurium Gram	Gram-atom	44. Thallium Gram	Gram-atom	45. Tin Gram	Gram-atom	46. Titanium Gram	Gram-atom	47. Tungsten Gram	Gram-atom
50° K	0.0288	3.67	0 0237	4.83	0.0286	3.40	0.0205	0.99	0.0095	1.75
100 K	0.0412	5.25	0 0279	5.69	0 0418	4.97	0 0455	2 19	0.0185	3.40
150 K	0.0455	5.80	0.0291	5 94	0.0472	5 62	0 0630	3.03	0 0243	4.47
200 K	0.0470	5.99	0.0300	6.13	0 0504	6 00	0.0775	3 73	0.0283	5.21
250 K	0.0475	6.06	0.0306	6 25	0.0527	6 27	0 0920	4.43	0.0310	5.70
0° C	0.0477	6 08	0.0309	6 30	0.0536	6 38	0 0985	4.74	0.0321	5.91
50	0.0482	6.15	0.0314	6.40	0.0554	6.59	0.1130	5 44	0.0338	6.22
100	0.0487	6.21	0.0319	6.50	0 0570	6.78	0.1275	6.14	0.0353	6.50
200	0.0496	6.32			0.0636	7.57	0 1565	7 53	0.0370	6.81
300	0.0505	6.43					0.1855	8.92	0.0383	7.05
400	0.0514	6.55					0 2145	10.32		
500										
600										
700										
800										
900										
1000										
Melting point	451°		301 7°		231 8°		1795°		3267°	
Solid	0.0519	6.62	(0.0338)	(6 90)	(0.0657)	(7.82)			0.0425	7.82
Liquid	—	—	—	—	0 0637	7.58	—	—	—	—
Average	—	—	0.0419	8.56	0.0768	9.14	—	—	—	—

TABLE 2—SPECIFIC HEAT (*Continued*)

Temperature	48. Zinc	
	Gram	Gram-atom
50° K	0.0400	2.61
100 K	0.0718	4.69
150 K	0.0844	5.52
200 K	0.0886	5.79
250 K	0.0910	5.95
0° C	0.0921	6.02
50	0.0941	6.15
100	0.0953	6.23
200	0.0996	6.51
300	0.1018	6.65
400	0.1030	6.73
Melting point	419.4°	
Solid	0.1033	6.75
Liquid	0.0956	6.25
Average	0.127	8.27

Table 3 contains additional values below 273° C for aluminum, carbon, copper, lead, magnesium, mercury, silicon, silver, sodium, sulphur, thallium and zinc.

1. Aluminum.—At low temperatures the values given by Nernst, Nernst and Schwers, Ewald, Koref, Tilden, and Schimpff, tend to run below Behn, Schmitz, Richards and Jackson, and Griffiths and Griffiths. Trowbridge and Nordmeyer are yet higher. The final curve is, therefore, a compromise, following Nernst and Schwers at low, agreeing fairly well with Behn, Schmitz, and Richards and Jackson, at higher, and at yet higher temperatures following Bontschew, and Griffiths and Griffiths, and Bailey. Schübel's results indicate a less rapid rise of the curve above 400° than the values given and his results may be correct. Slight extrapolation gives check results as follows for the total heat 90° K to 0° C:

Behn,	31.23 cals
Schmitz,	31.14 cals
Richards and Jackson,	31.65 cals
Curve given,	31.27 cals
Bailey, 0° to 600°,	146.9 cals
Curve given, 0° to 600°,	148.4 cals

TABLE 3

Absolute Temperature	Aluminium		Carbon				Copper		Lead	
			Graphite		Diamond					
	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom
10	—	—	—	—	—	—	$15.24° = 0.00077$	0.049	$\begin{cases}13° = 0.0054\\15° = 0.0084\end{cases}$	1.12 / 1.73
20	0.0026	0.07	0.0035	0.042	0.0	0.0	0.0017	0.11	0.0127	2.62
30	0.0077	0.21	0.0062	0.074	0.0	0.0	0.0063	0.40	0.0195	4.03
40	0.0196	0.53	0.0093	0.112	0.0	0.0	0.0127	0.81	0.0233	4.82
50	0.0347	0.94	0.0133	0.160	0.0008	0.010	0.0208	1.32	0.0251	5.20
60	0.0528	1.43	0.0178	0.214	0.0015	0.018	0.0299	1.90	0.0262	5.43
70	0.070	1.90	0.0225	0.270	0.0025	0.030	0.0382	2.43	0.0270	5.60
80	0.085	2.30	0.0275	0.330	0.0040	0.048	0.0469	2.98	0.0277	5.73
90	0.099	2.68	0.0335	0.402	0.0053	0.064	0.0547	3.48	0.0281	5.81
100	0.111	3.01	0.0400	0.480	0.0070	0.084	0.0620	3.94	0.0283	5.86
110	0.123	3.34	0.0460	0.552	0.0092	0.110	0.0678	4.31	0.0284	5.88
120	0.134	3.64	0.0530	0.636	0.0120	0.144	0.0720	4.58	0.0285	5.91
130	0.143	3.89	0.0600	0.720	0.0150	0.180	0.0752	4.78	0.0286	5.93
140	0.152	4.12	0.0663	0.796	0.0185	0.222	0.0776	4.93	0.0288	5.96
150	0.160	4.34	0.0735	0.882	0.0227	0.272	0.0794	5.05	0.0289	5.98
160	0.167	4.53	0.0805	0.966	0.0275	0.330	0.0810	5.15	0.0290	6.01
170	0.173	4.70	0.0878	1.054	0.0323	0.388	0.0823	5.23	0.0291	6.03
180	0.179	4.84	0.0951	1.141	0.0380	0.456	0.0834	5.30	0.0292	6.05
190	0.184	4.98	0.1024	1.229	0.0433	0.520	0.0845	5.37	0.0293	6.08
200	0.188	5.10	0.1097	1.316	0.0495	0.594	0.0854	5.43	0.0294	6.10
210	0.192	5.20	0.1170	1.404	0.0560	0.672	0.0865	5.50	0.0296	6.13
220	0.195	5.29	0.1243	1.492	0.0625	0.750	0.0873	5.55	0.0297	6.15
230	0.199	5.38	0.1316	1.579	0.0692	0.830	0.0882	5.61	0.0298	6.17
240	0.201	5.45	0.1389	1.667	0.0770	0.924	0.0889	5.65	0.0299	6.20
250	0.204	5.52	0.1462	1.754	0.0847	1.016	0.0895	5.69	0.0300	6.22
260	0.206	5.58	0.1535	1.842	0.0930	1.116	0.0901	5.73	0.0302	6.25
270	0.208	5.63	0.1560	1.872	0.1010	1.212	0.0908	5.77	0.0303	6.27
273	0.208	5.64			0.1030	1.236	0.0909	5.78	0.0303	6.28

TABLE 3 (Continued)

Absolute Temperature	Magnesium		Mercury		Silicon		Silver		Sodium	
	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom
3.45°			0.000534	0.11						
5.37°			0.00142	0.28						
10	—	—	0.0045	0.90	—	—	—		—	—
20	—	—	0.0115	2.30	0.001	0.03	0.0036	0.39	—	—
30	0.017	0.41	0.0188	3.77	0.004	0.11	0.0111	1.20	—	—
40	0.039	0.95	0.0228	4.57	0.009	0.25	0.0185	2.00	0.152	3.50
50	0.069	1.68	0.0249	4.99	0.016	0.45	0.0253	2.73	0.174	4.01
60	0.101	2.46	0.0262	5.26	0.024	0.68	0.0312	3.37	0.193	4.44
70	0.126	3.06	0.0272	5.46	0.034	0.96	0.0357	3.85	0.207	4.77
80	0.145	3.53	0.0279	5.59	0.044	1.25	0.0391	4.22	0.219	5.04
90	0.159	3.87	0.0284	5.70	0.054	1.53	0.0419	4.52	0.229	5.27
100	0.169	4.11	0.0289	5.80	0.063	1.78	0.0441	4.76	0.236	5.44
110	0.178	4.33	0.0294	5.88			0.0460	4.96	0.244	5.61
120	0.186	4.52	0.0297	5.96			0.0475	5.12	0.249	5.74
130	0.192	4.67	0.0301	6.03			0.0488	5.26	0.253	5.82
140	0.198	4.81	0.0304	6.10			0.0498	5.37	0.256	5.89
150	0.202	4.91	0.0307	6.16	0.099	2.80	0.0507	5.47	0.258	5.93
160	0.205	4.99	0.0310	6.23			0.0514	5.55	0.261	6.00
170	0.209	5.08	0.0314	6.30			0.0520	5.61	0.263	6.05
180	0.213	5.18	0.0317	6.37			0.0526	5.67	0.265	6.09
190	0.216	5.25	0.0320	6.43	0.128	3.62	0.0531	5.73	0.267	6.14
200	0.219	5.33	0.0323	6.48			0.0535	5.77	0.269	6.19
210	0.222	5.40	0.0326	6.54			0.0540	5.82	0.272	6.26
220	0.224	5.45	0.0328	6.59			0.0543	5.86	0.274	6.30
230	0.227	5.52	0.0331	6.64			0.0545	5.88		
			Liquid							
240	0.229	5.58	0.0338	6.79	0.151	4.27	0.0549	5.92	0.276	6.35
250	0.232	5.64	0.0337	6.77			0.0552	5.95	0.278	6.39
260	0.234	5.70	0.0336	6.75			0.0553	5.97	0.281	6.46
270	0.237	5.76	0.0335	6.73			0.0555	5.99	0.283	6.51
273	0.238	5.79	0.0335	6.72	0.160	4.53	0.0556	6.00	0.284	6.53

TABLE 3 (*Continued*)

Absolute Temperature	Sulphur				Thallium		Zinc	
	Rhombic		Monoclinic					
	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom	Gram	Gram-atom
10	—	—	—	—	—	—		
20	0.0245	0 79	—	—	0.0123	2.50	33.1° = 0.0191	1.25
30	0 0358	1 15	—	—	0.0178	3.63	0.0295	1.93
40	0 0455	1.46	—	—	0 0216	4.40	0.0400	2.61
50	0.0550	1 76	—	—	0.0237	4 83	0.0500	3.27
60	0.0640	2 05	—	—	0.0252	5.14	0.0573	3.75
70	0.0730	2.34	0.0850	2 73	0.0262	5 35	0.0632	4.13
80	0.0812	2.60	0.0925	2 97	0.0270	5.51	0.0675	4.41
90	0.0885	2.84	0 1000	3.21	0.0275	5.62	0 0718	4.69
100	0 0960	3.08	—	—	0.0279	5.69	0 0753	4.92
110	0.1020	3 27	—	—	0.0282	5 75	0 0784	5.13
120	0.1075	3 45	—	—	0.0284	5.80	0 0808	5.28
130	0.1128	3.62	—	—	0.0287	5 85	0.0828	5.41
140	0.1177	3.77	—	—	0.0289	5 90	0.0844	5.52
150	0.1222	3.92	0.131	4 20	0.0291	5 94	0.0856	5 60
160	0.1268	4 07	—	—	0.0293	5 98	0.0867	5.67
170	0.1308	4.20	—	—	0.0295	6 02	0.0874	5.71
180	0.1345	4.31	—	—	0.0297	6 06	0.0880	5.75
190	0.1382	4.43	—	—	0.0298	6 09	0.0886	5.79
200	0.1418	4 55	0.155	4.97	0.0300	6.13	0.0891	5.82
210	0.1452	4.66	—	—	0.0302	6.16	0.0895	5.85
220	0.1485	4 76	—	—	0.0303	6.18	0.0900	5.88
230	0 1520	4.87	—	—	0 0304	6.21	0.0905	5 92
240	0 1555	4.99	—	—	0.0305	6.23	0.0910	5.95
250	0 1585	5 08	0.170	5 45	0 0306	6.25	0.0914	5.97
260	0 1618	5.19	—	—	0.0307	6.27	0.0919	6.01
270	0 1648	5.29	—	—	0.0308	6.29	0.0921	6.02
273	0.1658	5.32	0.174	5 58	0.0309	6.30		

Roos extrapolates the values of Bontschew and of Schübel to cover the range from 18 to 657° and obtains values which for comparison I have changed to cover the range 0 to 658° and obtain as follows:

Bontschew,	167.8 cals
Schübel,	166.3 cals
Richards, J. W.,	158.3 cals
Pionchon,	160.5 cals
Curve given,	166.3 cals

2. Antimony.—The curve follows values of Dewar, Richards and Jackson, Rolla, Schübel, Schimpff, and Naccari, all fairly well. It is above Ewald at low and above Jahn at high and below Gaede, Dulong and Petit and Bede at high. The total of 34.46 calories obtained from the values given, 0° C to the melting point, agrees fairly well with the total 34.1 calories as given by J. W. Richards.

3. Argon.—There are no data as to the specific heat of the solid or liquid. For the gas see later.

4. Arsenic.—There are no determinations above 100° C. The curve below that point is very uncertain, being a compromise which might perhaps be considered a guess. The variety examined is not always mentioned but was supposed to be crystalline unless otherwise stated.

5. Bismuth.—Most of the determinations are in fair accord with the line given. Ewald is low, and as usual Bede and Stücker are wrong, and Naccari good. Jahn seems fair but not exact. Schübel's values indicate a total heat 0 to 271° of 8.34. The values given correspond to a total of 8.36.

6. Boron.—The specific heat of boron is considerably uncertain. The line adopted follows Dewar, Koref, Weber, etc., most nearly. The kind of boron used by Koref and by Dewar is not specified. The amorphous variety has a much higher specific heat than the crystalline judging from the determinations of Moissan and Gautier.

7. Bromine.—The determinations do not give the specific heat with any certainty. The total heat per gram of liquid bromine from the melting point to the boiling point is 7.527

cals, making the total heat in a gram of vapor at its boiling point from 0° K, 86.374 cals. For bromine as a gas see later.

8. *Cadmium.*—The curve follows Dewar, Griffiths and Griffiths, and Deuss fairly well except at the upper and lower ends of the curve by Deuss. It is not possible to say whether the extremely rapid rise in the curve after 450° K observed by Deuss is correct or not. The values of the specific heat given make the total heat, 0° to 321°, 18.78 calories, as against 18.13 found by Person. The values given by Deuss would make the total throughout this range more than 18.78 calories. Of course, the values given by Deuss at lower temperatures were extrapolated and are wrong.

9. *Caesium.*—The values for the specific heat given for caesium are uncertain. It would seem that the specific heat should decrease at low temperatures more than is shown, but the only determination at low temperatures that has been made (Dewar) was followed in arriving at the values given.

10. *Calcium.*—The values given follow the determinations of Dewar and Brunner. Bernini's values are lower and Nordmeyer's off.

11. *Carbon.*—For graphite the following values for the total heat 0 to 1000° C are indicated by the observations: Violle, 415 cals; Le Chatelier, 359.3 cals; Dewar, 301.4 cals; Kunz (charcoal), 356.3 cals; Weber, 377.5 cals. The values given correspond to a total heat of 380.2 calories for the same range of temperature. Above 1000° C one has to depend solely upon the observations of Violle. Magnus, after re-determining the specific heat of platinum, recalculates the results of Weber for diamond and graphite and gives equations good for 500° to 850° C (which cannot be extrapolated) which lead to values for graphite at 500°, of 0.388 and at 800°, of 0.434. The corresponding values for diamond are 0.383 and 0.428. Certainly the values given need readjustment, quite possibly so as to agree with the values as given by Magnus, but to attempt such readjustment with the data at hand would be largely guess work. The observations upon

diamond would indicate a total heat o to 1000° of 360.95 cals per gram.

The total heat of carbon per mol as vapor at its boiling point divided by the absolute temperature of the boiling point would be 44 from estimates that have been made.

12. Chlorine.—The values given for the specific heat of solid and liquid rest on the determinations of Dewar, Estreicher and Staniewski, and Knietsch, and are uncertain. As a gas see later.

13. Chromium.—The determinations by Mache, Adler, Richards and Jackson, Schimpff, Dewar, and Schübel seem to define the curve fairly well.

14. Cobalt.—The values for the specific heat given follow the determinations of Dewar, Schimpff, Tilden, Göbl, etc., most closely, these determinations being in fair accord. Tilden, Göbl, and Schübel all get discontinuity somewhere about 550° C. Probably the exact temperature at which discontinuity of the specific heat curve is evidenced depends upon the purity of the metal, as is certainly the case with iron. It is also possible that under carefully selected conditions the specific heat curves would remain regular near a discontinuity and there would be a sharp heat absorption (or evolution) at the temperature of discontinuity. Under ordinary circumstances the two phases of the metal do not seem to change suddenly the one into the other, and different observers get different results according to the method used. Probably the difference between the results of Göbl and Schübel, 400 to 600° C, is not due to inaccurate work. The estimated value of the total heat in solid at melting point is very uncertain.

15. Copper.—At low temperatures the values given follow Keesom and Onnes, Nernst, and Griffiths and Griffiths. From o to 1083° C the specific heat adopted is made to give the total heat found by J. W. Richards on the supposition of a linear variation of the specific heat from 100° C. This gives values in agreement with Glaser. For the total heat o to 600° C we have: Bailey 59.07; Schübel 59.50; curve given 60.99. Perhaps the curve should follow Harper and Schübel,

o to 600° with values as follows: 0° = 0.0905; 50° = 0.0924; 100° = 0.0940; 200° = 0.0966; 300° = 0.0993; 400° = 0.1014; 500° = 0.1043; 600° = 0.1080.

If these values are adopted the specific heat would have to increase rather rapidly above 600° in order to give a total heat at the melting point equal to that found by Ledebur, Richards and Frazier, or Glaser.

16. Glucinum.- -The determinations of Dewar and Humpidge are followed.

17. Gold.—The determinations of Dewar, Richards and Jackson, Schimpff, and Violle are mainly followed. Total 0° to melting point; Violle 34.49 cals; Roberts-Austen, 34.63 cals; curve given, 34.63 cals.

20. Iodine.- -The total heat added between o and 114° C according to the values given is 49.52 cals. The total heat observed throughout this range (slightly extrapolated) by Favre and Silbermann is 49.30 cals. The total heat per gram of the liquid from the melting point to the boiling point is 7.67 cals, making the total heat from 0° K to the vapor at its boiling point 60.91 cals.

21. Iridium.—The results given follow the determinations of Dewar, Behn and Violle mainly. The results o to 1400° C may be *badly wrong* if Violle's total heat for the solid at the melting point is correct. For, assuming the melting point to be 2290° C and assuming Violle's total and a linear variation of the specific heat, the specific heat at 1400° C would be 0.0382. At 2290° the specific heat would be 0.0426. Violle thought the melting point of iridium to be 1950° C.

22. Iron.—The values given for the specific heat of iron at low temperatures follow the results of Dewar, Ewald, and Griffiths and Griffiths, fairly well.

At 1530° C γ iron forms from the molten iron. At 900° C γ iron changes to β iron and probably gives out about 5.6 cals. At 760° C β iron changes to α iron and again gives out about 5.6 cals. α iron is commonly known as ferrite. The presence of carbon greatly complicates the relations, and the transformation temperatures, and the transformation and

specific heats, are also changed. A reference to a phase equilibrium diagram for iron and carbon will aid in understanding the changes that take place. The presence of carbon changes the specific heat of iron differently at different temperatures and concentrations of carbon. See Meuthen and Brown.

The specific heat for α iron increases regularly. This seems also to be true for the specific heat of β iron if due allowance is made for the heat evolved at the transformation points. The specific heat of γ iron is practically constant. Pionchon's results also indicate this. I regard Meuthen's determinations as the most accurate and they are in very close accord with the values adopted for the specific heat at high temperatures.

A summary of the most important data upon the total heat of iron at high temperatures is given in Table 4, and for comparison the total heat obtained from the values given for the specific heat of iron in Table 2. It will be seen that the assumption of a perfectly straight line for the specific heat of iron, o to 900° C, and of heat evolution at 760° and 900° as above stated, fits the facts excellently. The only point of possible criticism is at 700°, and as has already been pointed out, the exact transformation point depends upon the purity of the iron and the method of treatment.

23. Lead.—At low temperatures the values given follow the determinations of Eucken and Schwers, Keesom and Onnes, Griffiths and Griffiths, fairly well, and less closely those of Nernst. At higher temperatures, Griffiths and Griffiths, Gaede, Schübel, Magnus, and Naccari, are followed fairly closely. For the total heat o to 300° C we have Naccari 9.53; Spring 10.49; Magnus 9.586; Stücker 9.82; Schübel 9.589; curve given 9.585.

24. Lithium.—The values given for the specific heat follow Dewar, Koref, Laemmel, and Regnault, most closely. The determinations given by Bernini lie above the values adopted and those of Thum lie mainly below. The determinations differ widely. Thum's values o° C to the melting point would lead to a total of 163.35 calories, and those of Bernini

TABLE 4—TOTAL HEAT OF IRON BY DIFFERENT OBSERVERS

% Carbon	Pionchon <0.1	Pionchon corrected by Harker	Harker 0.01	Post	Euchêne	Oberhoffer 0.06
Temperature						
0, 100	—	—	—	10.8	11.0	—
0, 200	23.5[1]	23.5	23.5	22.0	23.0	—
0, 250	—	—	—	—	—	30.5
0, 300	36.8[1]	36.8	37.0	35.0	37.0	37.7
0, 400	51.6[1]	51.6	51.3	39.5[1]	42.0[1]	52.2
0, 500	68.2[1]	66.0	66.9	67.5	69.5	68.3
0, 600	87.0[1]	83.2	83.8	86.0[1]	84.0	85.0
0, 700	108.4[1]	102.2	104.1	108.0	106.0	111.8
0, 800	135.4[1]	125.0	127.8	132.0	131.0	135.8
0, 900	157.2[1]	146.7	148.0	157.0[1]	151.5	152.8
0, 1000	179.0	166.0	155.7	187.5	173.0	167.8
0, 1100		168.8				183.0
0, 1500						250.0

% Carbon	Meuthen 0 06	Beck	Stücker	Bailey 0.28	Schübel	Average	From values in Table 2
Temperature							
0, 100	—	—	11.2	—	—		10.95
0, 200	—	(22.8)	23.5	—	—	23.05	23.00
0, 250	—	—	—	—	—		29.44
0, 300	—	35.8	37.2	—	36.0	36 56	36.15
0, 400	—	49.9	52.9	47.0	49.7	50.51	50.40
0, 500	—	64.9	70.6[1]	62.0[1]	64.1	66.74	65.75
0, 600	82.37	80.5	93.7[1]	78.7[1]	81.5	82.55	82.20
0, 700	103.96	101.0	—	97.9	—	104.37	99.75
1, 800	129.38	124.9	—	126.9	—	129.10	129.60
0, 900	149.82	147.8	—	—	—	149.44	149.35
0, 1000							
0, 1100							
0, 1500							

[1] Not included in average. Bailey examined nine specimens of different composition; only his No. 7, a steel, is here given. There is a great variation in irons of different composition. The original articles must be consulted for details.

to 201.00 calories.   The curve given leads to a total over the same range of 177.21 calories.

25. *Magnesium.*—Above 0° C we have followed Schübel. His results are lower than the results given by Brunner or Stücker.   Reconciliation of the results does not seem possible. The values given lead to a total heat o to 650° C of 177.38. Roos' value of 179.3 is adopted in Table 5 because his heat of fusion is used.

26. *Manganese.*—The values given for the specific heat of manganese follow the determinations of Dewar, Estreicher and Staniewski, and Laemmel mainly.

27. *Mercury.*—The values given for the specific heat of solid mercury follow the determinations of Pollitzer and Onnes and Holst mainly.   The specific heat of the liquid follows the determinations of Barnes.   This curve shows a minimum of 0.03286 at 140° C.   For mercury as a gas see later.

28. *Molybdenum.*—The values given are very uncertain. They follow the determinations of Dewar, Richards and Jackson, and DeFacqz and Guichard.

29. *Nickel.*—The values given follow Dewar, Schimpff, Schübel, Tilden, Naccari, Schlett, etc., fairly well.   By slight extrapolation we obtain for the total heat:

	Euchene	Pionchon	Tilden	Bailey	Beck	Dumas	Schübel
0° to 600°	75.0	78.3	74 14	70.11	76.39	73.14	74.49
0° to 800°	103			97.79	104.9		
0° to 1000°	134						

Averaging Euchene, Tilden, Beck, Dewar, and Schübel, o to 600° we get 74.63 calories.   The curve given gives 74.67 calories.   The curve given gives 133.27 calories o to 1000° C. Schübel finds nickel constant from 380 to 630° at 0.125.

32. *Palladium.*—The values given follow the determinations of Dewar, Behn, Regnault, and Violle mainly.   Since Violle made the only determinations at high temperatures it seems as well to adopt his value for the heat of fusion and the total heat 0° C to the melting point and then correct the

specific heat given by Violle for his mistake in the melting point, making a linear variation in the specific heat throughout this interval. Violle thought that the melting point of palladium was 1500° C. Of course, this means that the specific heats as given at high temperatures are very uncertain.

33. Phosphorus.—-The values given partially follow the determinations of Dewar, Ewald and Heinrichs. It is impossible to reconcile the various results. The values of Wigand are much above those of Heinrichs. The results for yellow phosphorus would seem to be above those for the red, but beyond this fact the line for the yellow phosphorus is, if anything, less certainly established than is the line for the red. The transformation point of yellow to red phosphorus is 260° C and the heat of transformation has been variously determined. For phosphorus as a gas see later. The total heat of red·phosphorus o to 300° C = 57.57 cals.

34. Platinum.—From 500 to 1500° the values given follow the determinations of White. At o° C I thought the value adopted by White too high. The total value of the heat added, o° C to the melting point from the values given, is 65.71 calories. This value is to be compared with the value 75.21 calories obtained by Violle. The latter thought the melting point of platinum to be 1775° C. It is possible of course that the specific heat of platinum increases between 1500 and 1755° sufficiently to give on summation the total heat obtained by Violle, but this does not seem probable. For the total heat from o to 850° C, we have: White 29.89; Magnus 28.96; Violle 31.38; Bailey 28.72; Kunz 30.355; curve given 29.60. From o to 1200° C, we have: Pouillet 45.74; Violle 46.68; White 43.31; curve given 43.13.

35. Potassium.—The curve given follows Rengade at high temperatures. For potassium as a gas see later.

36. Rubidium.—There are not enough data to enable one to give the specific heat curve with any degree of certainty.

37. Selenium.—The determinations are too various to enable more than a guess to be made. If Dewar's values are

for crystallized selenium perhaps the guess made will be found
fairly correct.

38. Silicon.—Wigand says amorphous and crystallized
silicon are the same, the amorphous being micro-crystalline.
The differences in properties obtained he attributes mainly
to a difference in purity.

The values given follow Nernst, Schimpff, and at higher
temperatures Weber. They are in fair accord with Russell.
No determinations have been made for silicon above 232.4° C.
The total heat per gram from 0 to 250° C would be about
47.40 cals.

39. Silver.—The results at high temperatures for silver
are hard to reconcile. 6.00 for the atomic specific heat at
0° C seems to be pretty well established. Then Griffiths'
value at 97.44° C makes the line start well above that shown
by Tilden and Schübel, but is more in accord with Naccari,
Byström, and Pionchon. Pionchon's results give an average
0 to 960.5° of 0.0628 and if the line is straight this would be
equivalent to 6.76 at 500° C, which is a lower value than one
would expect from the trend of Griffiths and Griffiths' values.

Accordingly we give values below 0° C after Nernst,
and values above 0° so as to total, 0 to 600°, 35.33 calories.
Schübel gets for the same range 35.60, and Magnus 35.82
calories. After 600° we make the total heat agree with the
value given by Pionchon, no other determinations being
available.

40. Sodium.—The values given for sodium follow the
determinations of Dewar and Griffiths mainly. They are
below the values given by Bernini and Thum and only in fair
accord with Koref, and above Estreicher and Staniewski.
The specific heat of the liquid decreases to 0.318 at 140° C.
For sodium as a gas see later.

41. Sulphur.—Rhombic, monoclinic, and vapor of sul-
phur are in equilibrium at 95.5° C; liquid, vapor, and rhombic,
at 110.2° C; liquid vapor and monoclinic at 114.6° C. The
curves given give 2.806 calories for the heat of transformation
of rhombic to monoclinic at 100° C assuming their heat con-

tent to be equal at the absolute zero. The value for this transformation should be 3.36 according to Lewis and Randall. The heat of transformation of S_λ to S_μ is about 13 calories. This transformation occurs gradually, but much of the change takes place about 160° C.

The specific heat of monoclinic sulphur.. $= 0.174 + 0.00022t$
The specific heat of rhombic sulphur..... $= 0.168 + 0.00015t$
The specific heat of S_λ................ $= 0.21\ \ + 0.00016t$

The total heat from 100 to 390° from the formula for $S_\lambda = 72.2$ calories, which subtracted from the 76.47 calories observed from 100 to 390° gives 4.27 calories, against about 3.9 calories actually necessary to transform S_λ into S_μ. At 390° C the liquid sulphur is about 33.9 percent S_μ. At 100° C it is about 3.1 percent S_μ. See Lewis and Randall. 0.45 was added to the heat of fusion given by Lewis and Randall at 100° C to change the value to the heat of fusion at the melting point. The total heat of liquid sulphur per gram from the melting point to the boiling point is 88.9 grams for the rhombic and 87.9 grams for the monoclinic, making a total per gram of sulphur vapor from 0° K of 492.15 cals for the rhombic and 491.61 cals for the monoclinic.

42. Tantalum.—The curve follows Dewar, and Muthmann, Weiss and Riedelbauch. The determinations allow little more than a guess to be made. The specific heat probably increases from the values given at 100° C to about 0.04 in the neighborhood of 1300° C.

43. Tellurium.—The values given are very uncertain. They follow Dewar and Tilden. It is presumed that they used the crystalline tellurium.

44. Thallium.—The curve follows Nernst and Schwers, Dewar, Russell, Ewald, Richards and Jackson, and Schmitz fairly well. No determinations of the specific heat above 100° C have been made.

45. Tin.—The values given are for the white variety of tin and follow the determinations of Griffiths and Schübel at high temperatures.

46. *Titanium.*—The curve given is very uncertain. It follows Dewar and Nilson and Pettersson mainly.

47. *Tungsten.*—The curve given follows Dewar and De-Facqz and Guichard.

48. *Zinc.*—The values given follow Nernst, Pollitzer, Dewar, Griffiths and Griffiths, and Schübel. The values after 100° C are rather uncertain. From o to 419° C we have Schübel 41.64; Naccari 41.16; Person 39.68; much less from Ledebur; and from the curve given 41.45 calories.

Hydrogen.—For the specific he₁t of solid hydrogen only Kopp's estimate of 2.3 calories per gram obtained from a study of compounds is available. For the heat of fusion of hydrogen only Dewar's rou ;h ₁proximation of 16.0 calories per gram is available. For the specific heat of liquid hydrogen we have Dewar's determination of 3.4 calories per gram. The heat of vaporization of hydrogen is taken as 108.6 calories per gram in accord with Keesom's results.

For the specific heat of gaseous hydrogen from 35° K to 280° K the values given by Eucken as recorded in Table 5 are used. Eucken found that increasing the density of the hydrogen at low temperatures exerted an increasing effect upon the specific heat at constant volume. Hence Eucken calculated his results to an "ideal gas" condition. Eucken's results are remarkable in that they make diatomic hydrogen behave at low temperatures as an ideal monatomic gas so far as its specific heat is concerned. While I have adopted Eucken's values I feel very doubtful as to their correctness. For the effect of pressure on the specific heat of hydrogen as a gas the work of Joly and of Lussana must be consulted.

From 0° C upwards the true molecular specific heat of hydrogen would seem to be best represented by the equation

$$m\sigma_v = 4.78 + 0.0010t.$$

But various determinations are quite divergent and cannot be entirely reconciled, so that taking into account these variations we might write

$$m\sigma_v = 4.60 \text{ to } 4.90 + 0.0009t \text{ to } 0.0012t.$$

Oxygen.—For the specific heat of one gram atomic weight of solid oxygen we have again only the estimates of Kopp and of Meyer from a study of compounds as 4.0 to 4.9 calories. The heat of fusion of oxygen has not been measured. It is probably between 5.7 and 10 calories per gram. The specific heat of liquid oxygen has been given by Alt as 0.347 calories per gram. For the molecular specific heat at constant volume of oxygen as a gas we have

$$m\sigma_v = 4.90 + 0.0010t, \text{ or possibly } = 4.95 + 0.0012t.$$

Nitrogen. - For the specific heat of solid nitrogen we have a series of determinations by Keesom and Onnes, smoothed values being given in Table 5. Also they give the specific heat of the liquid per gram as 0.476 calorie. For the specific heat at constant pressure of nitrogen as a gas under 760 millimeters of mercury pressure see the values given in Table 5 after Plank and Holborn and Henning. The molecular specific heat of nitrogen as a gas above 0° C can be expressed fairly closely by the equation

$$m\sigma_v = 4.62 + 0.001065t.$$

TABLE 5

Hydrogen		Nitrogen		Nitrogen	
Temperature	$m\sigma_v$	Temperature	Atomic heat	Temperature	σ_p
35° K	2 99	15.27° K	1.60	77.33° K	0.2473
45	2.99	20	1.98	—150° C	0.2342
60	3.00	30	2 38	—100	0 2329
80	3 15	40	2.64	—50	0.2339
100	3.39	50	2.82	0	0 2354
120	3.68	60	2.89	50	0.2372
140	3.93	62.48	2.90	100	0 2390
160	4.15			200	0 2428
180	4.35			400	0 250
200	4.50			600	0 258
220	4.61			800	0.265
240	4.69			1000	0 273
260	4.75			1200	0.281
280	4.80			1400	0 288
				(1600	0 296)

TABLE 6

Element	Temperature	γ	Element	Temperature	γ	Element	Temperature	γ
Helium	−180, 18°	1.666	Hydrogen	−181°	1.597	Chlorine	16°	1.328
Neon	19	1.642		−76	1.453		320	1.314
Argon	0, 100	1.6675		16	1.407	Bromine	200	1.293
Krypton	19	1.689		15,532	1.389	Iodine	185.5	1.303
Xenon	19	1.666		15,689	1.374	Phosphorus	300	1.175
			Oxygen	−181	1.447			
				−76	1.416			
Sodium	750, 920	1.68		20	1.399			
Potassium	680, 1000	1.64	Nitrogen	−191	1.4778			
Cadmium	780, 900	1.669		0	1.4064			
Mercury	275, 356	1.666		500	1.4002			
				1000	1.3940			

Chlorine.—The molecular specific heat of chlorine gas at constant volume is given by the equation

$$m\sigma_v = 5.704 + 0.0005t$$

after Pier. The equation gives a value of 6.404 at 1400° C. Pier finds that chlorine commences to decompose above 1400° C.

Bromine.—The specific heat at constant pressure of bromine as a gas from 83 to 228° C has been determined by Regnault as 0.05518.

For the gaseous elements the best measurements that are available for the ratio of the two specific heats, γ, would lead to the values given in Table 6.

The values of γ for the monatomic gaseous elements are all in agreement with the theoretical ratio 5/3 for a monatomic gas to within the probable limit of experimental error. In similar agreement with the theoretical value of 2.979 for the specific heat at constant volume per gram molecular weight are the determinations for helium, —15 to 150° C, of 3.01, and for argon, 0 to 2500° C, of 2.977.

For the diatomic gases the values of γ show a decrease with a rise in temperature. The values of γ for the diatomic gases seem also to depend upon the pressure, for Valentiner gives for nitrogen the equation at 82° K,

$$\gamma = 1.3997 + 0.07812P/S,$$

where P/S is the ratio of the actual to the saturation pressure.

Phosphorus as a vapor has 4 atoms in its molecule.

In Tables 7 and 8 are given for convenient reference the atomic weights used, also the melting points, boiling points, heats of fusion and heats of vaporization adopted as best representing the best measurements that have been made. Also using the data given in this paper in these tables are given the total heat added to the respective elements from 0° absolute to 0° C, and from 0° C to the melting points of the elements, and the total heat from 0° absolute in the element both as a solid and as a liquid at its melting point. Finally the total heat per gram atomic weight for the element in the liquid

TABLE 7

Element	Atomic weight	Melting point		Boiling point		Kinetic energy per gram atomic weight		Total heat at 0°C		Heat of vapor- ization per gram
		T°C	T°K	T°C	T°K	Melting point	Boiling point	Per gram	Per gram atomic weight	
1 Aluminum	27.10	658	931	1800	2073	2774	6178	34.5	935	1771
2 Antimony	120.2	630	903	1440	1713	2691	5105	10.01	1203	—
3 Argon	39.88	Triple point −189.3	83.7	−185.83	87.17	249.4	259.8	—	—	38.8
4 Arsenic	74.96	500	773	616	889	2304	3532	14.30	1072	—
5 Bismuth	208.0	270.95	543.95	1420	1693	1621	5045	6.69	1392	198.9
6 Boron	11.0	Volatile in arc		Volatile in arc		—		24.02	264	—
7 Bromine	79.92	−7.3	265.7	63.05	336.05	792	1001	33.63	2688	46.0
8 Cadmium	112.40	320.9	593.9	765.9	1038.9	1770	3096	11.73	1319	209.7
9 Caesium	132.81	28.45	301.45	670	943	898	2810	13.58	1803	—
10 Calcium	40.07	803	1076	—		3207	—	32.32	1295	—
11 C { Diamond Graphite	12.00	Volatile in arc		3600	3873	—	11542	Liquid 8.13 / 17.32	97.5 / 207.8	12033
12 Chlorine	35.46	−103.5	169.5	−33.7	239.3	505	713	Gas 130.28	4620	69.2
13 Chromium	52.0	1550	1823	2200	2473	5432	7370	15.91	827	—
14 Cobalt	58.97	1478	1751	—		5218	—	16.44	970	—
15 Copper	63.57	1083	1356	2310	2583	4041	7697	16.65	1058	1104

TABLE 7—(Continued)

Element	Atomic weight	Melting point T° C	Melting point T° K	Boiling point T° C	Boiling point T° K	Kinetic energy per gram atomic weight Melting point	Kinetic energy per gram atomic weight Boiling point	Total heat at 0° C Per gram	Total heat at 0° C Per gram atomic weight	Heat of vaporization per gram
16 Glucinum	9.1	Under 1000	1273	—	—	3794	—	—	—	—
17 Gold	197.2	1062.4	1335.4	2200	2473	3980	7370	6.66	1314	395.5
18 Helium	3.99	—272 (Triple point)	1	—268.71	4.29	2.98	12.78	—	—	4.99
19 Hydrogen	1.008	—259.05	13.95	—252.67	20.33	41.6	61.9	917.1	925	108.6
20 Iodine	126.92	113.5	386.5	184.35	457.35	1152	1363	11.39	1445	23.95
21 Iridium	193.1	2290	2563	—	—	7638	—	5.83	1126	932
22 Iron	55.84	1530	1803	2450 (Above)	2723	5373	8115	16.88	943	—
23 Lead	207.1	327.4	600.4	1525 (Above)	1798	1789	5358	7.14	1480	211.0
24 Lithium	6.94	180.0	453.0	1400	1673	1350	4986	115.72	803	—
25 Magnesium	24.32	650	923	1120	1393	2751	4151	44.09	1072	1933
26 Manganese	54.93	1260	1533	1900	2173	4568	6476	18.48	1015	—
27 Mercury	200.6	—38.85	234.15	356.95	629.95	698	1877	10.35 (Liquid)	2075	67.8
28 Molybdenum	96.0	2535	2808	—	—	8368	—	10.59	1017	—
29 Nickel	58.68	1452	1725	2400	—	5140	—	16.78 (Gas)	985	—
30 Nitrogen	14.01	—210.52	62.48	—195.67 (20 mm)	77.33	186.2	230.4	123.82 (Gas)	1735	47.75
31 Oxygen	16.00	—218.4	54.6	—182.8	90.2	162.7	268.8	121.55 (Gas)	1945	50.92

TABLE 7—(Continued)

Element	Atomic weight	Melting point		Boiling point		Kinetic energy per gram atomic weight		Total heat at 0°C		Heat of vaporization per gram
		T°C	T°K	T°C	T°K	Melting point	Boiling point	Per gram	Per gram atomic weight	
32 Palladium	106.7	1549.2	1822.2	—	—	5430	—	11.05	1179	947
33 P { Red	31.04	44.0	317.0	289	562	945	1675	30.25	939	130.4
Yellow								36.02	1118	650.6
34 Platinum	195.2	1755	2028	—	—	6043	—	6.415	1252	—
35 Potassium	39.10	63.5	336.5	762.2	1035.2	1003	3085	39.47	1543	—
36 Rubidium	85.45	39.0	312.0	696	969	930	2888	19.64	1678	—
37 Se { Amorphous	79.2									—
Crystalline		217	490	688	961	1460	2864	14.79	1171	—
38 Silicon	28.3	1414	1687	—	—	5027	—	22.45	635	—
39 Silver	107.88	960.9	1233.9	1955	2228	3677	6639	10.92	1178	531.0
40 Sodium	23.00	97.9	370.9	882.9	1155.9	1105	3445	59.07	1359	—
41 S { Rhombic	32.07	110.2	383.2	444.45	717.45	1142	2138	28.64	919	—
Monoclinic		114.6	387.6			1155		30.46	977	—
42 Tantalum	181.5	2850	3123	—	—	9306	—	6.51	1181	339.9
43 Tellurium	127.5	451	724	1390	1663	2158	4956	10.41	1327	—
44 Thallium	204.0	301.7	574.7	1280	1553	1713	4628	9.76	1458	—
45 Tin	119.0	231.8	504.8	2275	2548	1504	7593	10.94	1301	597.1
46 Titanium	48.1	1795	2068	—	—	6163	—	14.81	712	—
47 Tungsten	184.0	3267	3540	—	—	10549	—	5.53	1018	—
48 Zinc	65.37	419.4	692.4	918	1191	2063	3549	18.66	1220	417.6

TABLE 8

TOTAL HEAT

| Element | Heat of fusion per | | 0° C to melting point | | 0° K to melting point | | | | Total/T |
| | | | | | Solid | | Liquid | | |
	Gram	Gram atomic weight	Gram	Gram atomic weight	Gram	Gram atomic weight	Gram	Gram atomic weight	
1 Aluminum	82.0	2222	166.3	4507	200.8	5442	282.8	7664	8.23
2 Antimony	40.2	4832	34.46	4142	44.47	5345	84.67	10177	11.27
5 Bismuth	12.39	2577	8.36	1739	15.05	3131	27.44	5708	10.49
7 Bromine	16.185	1294	—0.781	—62.4	16 66	1332	32.85	2625	9.88
8 Cadmium	13.7	1540	18.78	2111	30 51	3429	44.21	4969	8.36
9 Caesium	3.76	499	1.596	212	15.17	2015	18.93	2514	8.34
11 Carbon	—	—	2050	24600	2067	24808	—	—	—
12 Chlorine	22.96	814	—	—	19.32	685	42.28	1499	8.84
14 Cobalt	—	—	227.4	13 410	243.8	14380	—	—	—
15 Copper	43.3	2753	118.7	7.546	135 35	8604	178.65	11357	8.37
17 Gold	16.3	3214	34 63	6829	41 29	8143	57.59	11358	8.50
19 Hydrogen	16 0	16.13	—	—	32 08	32.3	48.08	48.46	3.47
20 Iodine	11.71	1486	6.19	786	17 58	2231	29.29	3717	9.61
21 Iridium	—	—	84 5	16317	90.33	17443	—	—	—
22 Iron	69 0	3853	254 5	14212	271.4	15154	340.4	19008	10.54
23 Lead	5 345	1107	10 51	2176	17.65	3656	23.00	4763	7.93
24 Lithium	32.81	228	177.2	1230	292.9	2033	325.7	2261	4.99

Liquid

TABLE 8—(Continued)

TOTAL HEAT

| Element | Heat of fusion per | | 0° C to melting point | | 0° K to melting point | | | | Total/T |
| | Gram | Gram atomic weight | Gram | Gram atomic weight | Solid | | Liquid | | |
					Gram	Gram atomic weight	Gram	Gram atomic weight	
25 Magnesium	72.0	1751	179.3	4360	223.4	5432	295.4	7184	7.78
27 Mercury	2.785	558.6	—1.314 (Liquid)	—263.6	6.25	1254	9.036	1813	7.74
30 Nitrogen	13.7	191.9	—	—	9.22	129.24	22.92	321.1	4.15
31 Oxygen	(5.70)	(91.2)	—	—	13.65	218.4	19.35	309.6	5.67
32 Palladium	36.3	3873	109.8	11716	120.8	12895	157.15	16768	9.20
33 Phosphorus	5.02	156	7.942	247	43.97	1365	48.99	1521	4.80
34 Platinum	27.18	5305	65.71	12826	72.13	14078	99.31	19386	9.56
35 Potassium	14.63	572	11.566	452	51.03	1995	65.66	2568	7.63
36 Rubidium	6.15	526	3.356	287	22.99	1965	29.14	2490	7.98
37 Selenium	—	—	19.964	1581	34.75	2752	—	—	—
39 Silver	24.72	2667	60.32	6507	71.24	7685	95.96	10352	8.39
40 Sodium	27.37	630	29.25	673	88.32	2031	115.69	2661	7.17
41 S { Rhombic	—15.32	491	19.392	622	48.03	1540	63.35	2032	5.30
41 S { Monoclinic	11.96	384	21.39	686	51.85	1663	63.81	2046	5.28
43 Tellurium	—	—	22.49	2867	32.90	4194	—	—	—
44 Thallium	7.2	1469	7.145	1991	16.91	3449	24.11	4918	8.56
45 Tin	14.23	1693	13.62	1621	24.56	2922	38.79	4616	9.14
48 Zinc	27.45	1794	41.446	2709	60.11	3929	87.56	5724	8.27

condition at its melting point divided by the absolute temperature of the melting point is given under the heading Total/T. The extrapolations of the data involved in obtaining the total heats given in Tables 7 and 8 will introduce no serious error if the data already given are correct.

The facts which have been presented in this paper permit many interesting conclusions to be drawn. These will be discussed in a continuation of this article.

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   Columbia, S. C.
      Feb. 15, 1917

QUANTITATIVE LIGHT-FILTER FOR THE ULTRA-VIOLET PART OF THE SPECTRUM[1]

BY N. P. PESKOV

The question of obtaining monochromatic light within narrow limits of wave-lengths is important both from the theoretical and the practical standpoint. The following practical methods are in existence:

(1) Coloration of the flame with vapors of different metals. This is the least perfect method.

(2) Rubens' method of "residual rays" based on selective reflection of light by different substances.

(3) Spectroscopical method. This is the most accurate, but on account of the very small intensity of light can hardly be applied to photochemical reactions.

Finally, there is a method of filtration through absorbing media or light-filters. This method has so many advantages as compared with the others, that it is used in almost all photochemical investigations where monochromatic light is needed. Formerly the light-filters were used only for the visible part of the spectrum, and they were of more or less qualitative nature. With the development of photochemistry, however, a need for more accurate filters has arisen, and there came into existence so-called "quantitative" light-filters, *i. e.*, filters through which only rays of definite, previously calculated, wave-lengths can pass. In order to prepare such a light-filter it is necessary to calculate the coefficient of absorption of the substance or substances used for the filter. Knowing this coefficient we can calculate the concentration of the substance and the thickness of layer required to get light of definite and known wave-lengths. The formulae for these calculations are very simple. According to Beer's law the intensity of light entering the filter (I_o) and the in-

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tensity of light transmitted through the filter (I_x) are connected by the following equation:

$$I_x = I_o \cdot 10^{-EXC} \tag{1}$$

where C is the concentration of the substance and X the thickness of the layer.

From this equation

$$E = \frac{1}{CX} (\log I_o - \log I_x). \tag{2}$$

The physical meaning of the coefficient E is this. At a concentration equal to 1 the value $\frac{1}{E}$ will express in centimeters the thickness of layer necessary to decrease the intensity of light ten times. For instance, E for iodoform for rays of wavelength $\lambda = 436 \ \mu\mu$ equals 21.4. This means that a normal solution of CHI_3 with a thickness of layer $1/21.4$ cm will decrease the intensity of light of this wave-length ten times.

From Equation 1 it is easy to determine the quantity of light emerging from the filter expressed in percentage of light entered. From Equation 1 follows

$$\frac{I_x}{I_o} = 10^{-EXC}. \tag{3}$$

Hence the percentage of light (p) transmitted through the filter

$$p = \frac{I_x}{I_o} \cdot 100 = 10^{-EXC} \cdot 10^2 = 10^{2-EXC}. \tag{4}$$

As long as the problem of the preparation of light-filters was limited to the visible part of the spectrum it was a comparatively simple matter. In this case the coefficient of absorption could be determined with great accuracy by means of a good spectrophotometer. But as soon as we pass to the region of shorter wave-lengths the matter becomes more complicated. Our eye is not sensitive in this part of the spectrum, and we have no physiological criterion for the comparison of absorbed and transmitted rays. On the other hand, it is very important to be able to separate the ultraviolet part of the spectrum from the visible part, and different regions of ultraviolet light from each other, in view of the fact that

many inorganic and very many organic substances possess a selective absorption and photochemical sensitiveness in the ultraviolet part of the spectrum.

The separation of the ultraviolet part of the spectrum from the visible had been done by several investigators. Wood[1] used for this purpose a thin plate of metallic silver, or celluloid diaphragm colored with nitrosodimethylaniline. The latter substance was also used by Lehmann[2] for construction of his apparatus giving exclusively ultraviolet light. The principle of the apparatus is to concentrate by means of quartz lenses light from a source rich in ultraviolet rays and pass it through a series of media absorbing all visible rays. As media, Lehmann used blue U. V. glass, solution of $CuSO_4$ and solution of nitrosodimethylaniline. The light passing through this apparatus was invisible to the eye, but could be detected by chemical action and especially by the phenomena of phosphorescence and fluorescence, for investigations of which the apparatus was constructed. Neither investigator paid much attention to the quantitative side of the problem.

It was my object to find a light-filter absorbing the entire region of the spectrum between 500 and 300 $\mu\mu$ and to study this absorption quantitatively by varying the concentration and thickness of layer of the filter. I first studied the substances used by Wood and Lehmann, *viz.*, silver and paranitrosodimethylaniline. Photographs taken through these substances showed, however, that rays in the region 360–300 passed easily through these media. There was, however, a possibility of using those substances together with some other substance absorbing the long ultraviolet rays. Paranitrosodimethylaniline was not good for this purpose, since photographs showed it to be transparent for wave-lengths 200–250 $\mu\mu$, as was also found by Defregger.[3] Organic dyes and other complex organic compounds are not suitable for my purposes

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[1] Phil. Mag., (6) 3, 607 (1902); Proc. Am. Ac., 39, 51 (1903); Astrophys. Jour., 17, 133 (1903).

[2] Verh. deutsch. phys. Ges., 12, 890 (1910); Phys. Zeit., 11, 1039 (1910); Zeit. Instrumentenkunde, 32, 43 (1912).

[3] Drude's Ann., 41, 1012 (1913).

since all of them have more or less distinct absorption bands in the region of the shortest ultraviolet rays. I, therefore, tried to find the desired substance among simpler compounds, and have chosen chlorine, since the data in the literature[1] showed that chlorine is transparent for short ultraviolet waves. Photographs taken by myself not only confirmed these data, but also showed that chlorine is the right substance for our purposes, since the maximum absorption for chlorine is in the region 380–300 $\mu\mu$.

Next I had to find another substance absorbing the region 500–380 $\mu\mu$. Silver was known as an absorbent of visible rays. I have not chosen metallic silver, however, as a majority of investigators[2] did, but colloidal silver. The practical advantage of it is that one can regulate the concentration and thickness of the layer much more easily than when dealing with metallic plates. Besides, metallic silver is perceptibly transparent for blue and violet rays while a colloidal solution of silver is not. Especially good results were obtained with silver reduced and deposited as a colloid in a gelatine diaphragm. Diaphragms of brownish red color were obtained this way. Photographs taken through such diaphragms and solutions of colloidal silver showed, however, that the absorbing capacity ends at about 400 $\mu\mu$, *i. e.*, before the region of chlorine absorption begins. With increase of concentration considerable absorption in the region of short ultraviolet rays is noticeable. It appears, therefore, that silver is just as unsuitable as nitrosodimethylaniline for our light-filter.

I then turned my attention to bromine whose spectrum was more than once investigated qualitatively.[3] Photographs

[1] W. H. Miller: Phil Mag., (3) **2**, 381 (1883); W. A. Miller: Ibid., (3) **27**, 81 (1845); Moureu: Comptes rendus, **49**, 606 (1859); Liveing and Dewar: Proc. Roy. Soc., **35**, 71 (1883); Laird: Astrophys. Jour., **14**, 85 (1901).

[2] Stokes. Phil. Trans., **152**, II (1862); Cornu: Ann. sci. école norm. Sup., **9**, 21 (1880); Wernicke: Pogg. Ann., Erg. Bd., **8**, 55 (1876); Liveing: l. c.; Rubens and Hagen: Drude's Ann., **8**, 432 (1902); Minor: Ibid., **10**, 581 (1903).

[3] W. H. Miller: l. c.; W. A. Miller: l. c. and Phil. Trans., **152**, I, 681 (1863); Roscoe and Thorpe: Phil. Trans., **167**, 207 (1876); Martens: Verh. deutsch. phys. Ges., **4**, 138 (1902).

taken through vapors of bromine gave very satisfactory re-
sults. For the entire ultraviolet part of the spectrum be-
ginning from 380 $\mu\mu$, bromine is transparent, and at the
same time it cuts out the entire visible part of the spectrum
up to 380 $\mu\mu$, *i. e.*, its absorption capacity ends a little bit
beyond the point where the absorption by chlorine begins.

All these data are given in Fig. 1, where the dark lines
represent the absorption regions of the substances investigated
and the heavy line on the
bottom of the diagram corre-
sponds to the region of wave-
lengths we want to eliminate.
The two lines for silver corre-
spond to two plates of different
thickness. It is clear from the
diagram that only Cl and Br
have absorption bands covering
our region without any gap. I
decided, therefore, to use Cl and
Br for my light-filter. The
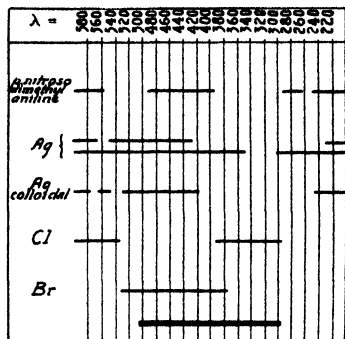
Fig. 1

question now arises how to use these elements, whether as
gases, or as solutions, *e. g.*, in water. Photographs through
solutions of Cl and Br in water gave interesting results, *viz.*,
their spectra were quite different from those of gaseous Cl and
Br. The difference might be ascribed to formation of complex
molecules of halogen and water. Anyway for our purposes
gaseous Cl and Br had to be used, as only their absorption
spectra answer our requirements.

Before passing on to quantitative determination of the
absorbing capacity of mixtures of Cl and Br, I tested them
out as a light-filter in an experiment analogous to that of Leh-
mann. Rays from an arc light between copper and iron passed
through a mixture of Cl and Br, which was in a vessel with
quartz windows. Only red and a very small part of yellow
and green rays remained visible for the eye. Solution of aescu-
lin in a quartz vessel placed in the path of these rays showed
strong fluorescence. It is easy to prove that this fluorescence

is not caused by the visible rays. A screen of transparent glass placed between the light filter and the solution caused disappearance of fluorescence, although the visible rays passed freely through the screen. It is evident then that in our experiment, as in Lehmann's, the fluorescence is caused by the ultraviolet rays which pass through the light filter. But it is easy to show that the ultraviolet rays of Lehmann's experiment and mine belong to different regions of the ultraviolet part of the spectrum. A quartz vessel with a solution of $CuSO_4$ placed in the path of rays emerging from my light-filter does away with the fluorescence, while Lehmann used this solution for filtering his light without doing away with the fluorescence. It is plain then that only short ultraviolet rays pass through a mixture of Cl and Br.

Now I had to determine quantitatively the coefficients of absorption for Cl and Br for different wave-lengths. Since the determinations had to be done in the ultraviolet region of the spectrum I could not make use of the spectrophotometer. I availed myself of the photographic method of Henri.[1] This method consists in taking photographs of a series of spectra through the absorbing substance and without it, one after another. The time of exposure without the absorbing medium is constant (t_0), with the absorbent it varies within a considerable interval (t_x). We have, therefore, for every absorption spectrum one plain spectrum (comparison spectrum). Then for each line of the spectrum of our source of light we find two adjoining photographs (of absorption and comparison spectra) on which the given line has the same intensity of the image. The time of exposure of both photographs is known. Schwarzschild's[2] formula gives a simple relation between the time of exposure and intensity of light in case of equal intensities of the image.

$$\frac{I_x}{I_0} = \left(\frac{t_0}{t_x}\right)^n = 10^{-ECX} \tag{5}$$

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[1] Comptes rendus, **153,** 265, 535, 1629 (1911); Jour. de Phys. (1913); Phys. Zeit., **14,** 516 (1913).

[2] Jahrbuch der Photographie, **1900,** 161.

Hence, the coefficient of absorption

$$E = \frac{n}{CX} (\log t_z - \log t_o) \qquad (6)$$

where n is a constant dependent on the kind of photographic plate. It varies between 0.8 and 1 and has to be calculated in advance. Henri worked with Wratten's plates and found $n = 0.9$. My own measurements for the same plates by J. S. Plotnikov's method[1] with Krüss' colorimeter gave for n the value 0.87, which was used in my calculations.

The difficulty of Henri's method consists mainly in the determination of the relative intensity of the image on the photographic plate. Henri used for this purpose a microphotometer, but this does not exclude purely physiological difficulties. The eye gets tired very quickly when differentiating between lines of different intensity. Besides, the lines subject to investigation are of different width, and this necessarily leads to an optical illusion in choosing lines of the same intensity of color. I studied the photographs through a black screen with a transparent slot so that the lines were observed as having the same width. This is not as accurate as Henri's method but much simpler and sufficient for quantitative characterization of the light filter. In his experiments, Henri had on one plate 45 spectra (23 absorption and 22 comparison spectra). The large number of spectra allowed variation in time of exposure and resulted in greater accuracy. I had on my plate 54 spectra arranged so that after two absorption spectra one comparison spectrum followed. In this way I also had absorption and comparison spectra adjoining each other and at the same time the number of absorption spectra was increased to 34.

In my method I also met with a difficulty in determining the concentrations of gaseous Cl and Br in my light-filter. When Cl and Br were used in separate vessels they could be absorbed by a solution of KI and titrated with hyposulphite. From a series of observations on filling the vessel with Cl,

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[1] J. S. Plotnikov: Photochemical Researches, 2nd part, Moscow, 1915.

I concluded that the amount of Cl could be calculated with sufficient accuracy from barometric and temperature data. Analogous calculations for Br did not give good results and Br was determined either by titration or as AgBr. When the absorbing vessel was filled with a mixture of Cl and Br the quantity of each component was determined by the Jannasch-Claasen method. Both Cl and Br were precipitated as AgCl and AgBr, filtered through asbestos and heated in a stream of Cl to transform all the AgBr into AgCl. Or AgCl and AgBr are reduced with zinc dust and H_2SO_4, KOH added, Br precipitated with $KMnO_4$, sulphuric and acetic acid added, Br absorbed with KI and titrated with hyposulphite. The following results were obtained by these methods. Using the first method I found AgCl + AgBr = 0.09406 g. After heating in a stream of Cl, 0.08872 g. Difference D = 0.00534 g. Atomic wt. of Cl = 35.45, Br = 79.96. Molecular wt. of AgCl = 143.38, AgBr = 187.89. Difference AgBr — AgCl = 44.51. The amount of Br(x) is calculated from the proportion.

$$\frac{x}{79.96} = \frac{D}{44.51} \quad x = 0.009364 \text{ g.}$$

The volume of the vessel containing Br was 41 cc. Hence, the molar concentration of Br is C_{Br} = 0.002402. Knowing the amount of Br in the mixture AgCl + AgBr it is easy to calculate the amount of Cl; it is 0.017805 g. The volume of the vessel containing Cl was 86 cc. Hence, the molar concentration of Cl is C_{Cl} = 0.02189.

The second method gave the following results: AgCl + AgBr = 0.70273. After reducing with Zn dust and separation of Br, the latter was absorbed by 50 cc of solution of KI. The solution was then diluted to 100 cc, and 10 cc of it were titrated with $N/100$ solution of hyposulphite. Five titrations gave following results: 8.26 cc, 8.19 cc, 8.20 cc, 8.24 cc, 8.21 cc. Average, 8.22 cc. From this the amount of bromine separated = 0.06574 g. Cl could be determined by difference, but I also verified the results by precipitating it again as AgCl.

N. P. Peskov

TABLE I

E_{Cl}			Wave-length of a quartz lamp λ	E_{Br}		
Expt. I	Expt. II	Average value		Average value	Expt. I	Expt. II
8.1	7.7	7.9	579.0	17.5	17.1	17.9
6.3	5.7	6.0	546.0	37	38.3	36.3
—	—	—	496.0	50	48.4	51.2
14.7	15.3	15	435.9	189	185.7	192
20	21.0	20.5	410.0	—	—	—
26.4	27.6	27	404.8	162	160	165
—	—	—	398.4	—	—	—
18.4	17.6	18	390.6	140.1	138.6	142.6
14.9	15.5	15.2	386.0	—	—	—
17.7	18.3	18	382.0	—	—	—
20.4	21.2	20.8	379.1	115	113.4	118
32.2	33.8	33	375.0	112	113.4	110
—	—	—	370.0	—	—	—
39.1	37.3	38.2	365.0	100	98	102
—	—	—	359.2	—	—	—
45	43	44	356.0	72	73.5	70.5
50.2	52.8	51.5	339.1	68	67.1	69.7
53	55	54	334.3	—	—	—
44.6	42.4	43.5	313.0	63	62.5	64.5
31.1	32.9	32	302.0	53	54.3	51.7
21.5	20.5	21	296.7	47.2	48.4	46
19.6	18.8	19.2	292.5	48	51.4	46.8
17.4	16.8	17.1	289.3	41	41.8	40
16.8	16.2	16.5	287.2	—	—	—
—	—	—	282.1	—	—	—
13.1	12.5	12.8	280.6	37.2	38.3	37
9.2	8.8	9	275.9	30.1	30.6	29.7
8.3	7.9	8.1	270.1	—	—	—
7.5	7.5	7.5	267.7	—	—	—
7.5	6.5	7	265.0	33.2	38.3	34
7.2	6.8	7	264.1	42.1	41.8	41.1
7.2	6.8	7	262.6	37.5	38.3	38.4
—	—	—	261.1	—	—	—
—	—	—	257.5	—	—	—
4.6	4.6	4.6	253.6	35.8	34.6	37
—	—	—	249.5	—	—	—
4.0	4.4	4.2	245.2	—	—	—
—	—	—	241.3	—	—	—
—	—	—	238.6	—	—	—
6.1	5.9	6	234.7	36.5	34.6	37
6.2	5.8	6	232.6	37	38.3	37.7
6.1	5.9	6	230.8	38	38.3	38.4
6.1	5.9	6	226.3	40.3	41.8	39.8

Now I proceed with the determination of the coefficient of absorption for Cl and Br. For this purpose I made several photographs of absorption spectra of Cl, Br, and mixtures of both. Besides, using a double quartz vessel I filled one compartment with Cl, the other with Br, then took photographs through this vessel, once when the compartments were separated, and the other time when they were connected by means of a stop-cock, and the gases were diffused. This latter experiment was both of theoretical and practical interest. Having calculated the results obtained from photographs through separated and connected components I proved experimentally the correctness of my supposition, that a mixture of Cl and Br must follow Beer's law, *i. e.*, no molecular change takes place on mixing of the two gases, either on account of change of concentration or chemical action between Cl and Br. Photographs were taken at different concentrations and different time of exposure both for absorption and comparison spectra. The results of calculation showed that the values for coefficients of absorption obtained from different experiments differ not more than 5 percent. The values for the absorption coefficient of Cl and Br are given in Table I.

In Fig. 2 are given the absorption curves for Cl and Br. From the cut we can see that these elements are suitable for our light-filter, and we also can judge approximately as to the relative concentrations of Cl and Br required to produce the desirable results.

To give a clearer idea about calculation of absorption coefficients from the photographs I shall show here how the values for E_{Br} in Table I were calculated. The time of the exposure
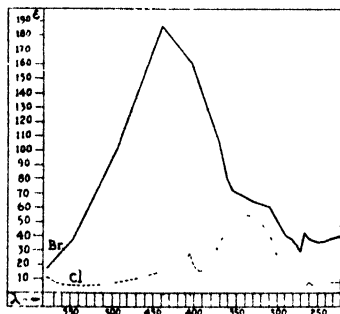
Fig. 2

varies from 6.5 to 120 seconds. For the comparison spectrum it was 5 seconds. In the following table (II) under λ are

N. P. Peskov

TABLE II

$t_0 = 5$ seconds / t_x	λ	E_{Br}
6.5	579.0	17.1
7	—	—
7.5	—	—
8	275.9	30.6
8.5	253.6; 238.6	34.6
9	546.0; 280.6; 265.0; 262.6; 232.6; 230.8	38.3
9.5	289.3; 264.1; 226.3	41.8
10	—	—
10.5	496.0; 296.7	48.4
11	292.5	51.4
11.5	302.0	54.3
12	—	—
12.5	—	—
13	313.0	62.5
14	339.1	67.1
15.5	356.0	73.5
17	—	—
20	—	—
22.5	365.0	98.0
25	—	—
28.5	379.1; 375.0	113.4
32	—	—
35	—	—
38.5	—	—
42	390.6	138.6
46	—	—
51	—	160.0
57.5	404.8	—
64	—	—
71	—	—
77	—	—
87	435.7	185.7
100	—	—
120	—	—

given those lines of the spectrum of the quartz lamp, which gave the intensity of the image equal to that on the comparison spectrum. E_{Br} was calculated from Equation 6.

$$ E = \frac{n}{CX} (\log t_x - \log t_0) $$

In our case $n = 0.87$, concentration $C_{Br} = 0.00439$, thickness

of layer $x = 1.29$, and $t_o = 5$. Substituting all these values in the formula, and also corresponding values for t_x, we will get E_{Br}. For exposure of 42 seconds, for instance, the line of the spectrum corresponding to 390.6 $\mu\mu$ gave the same intensity of the image as on the comparison spectrum. The absorption coefficient for this line of the spectrum is calculated as follows:

$$E_{Br}^{390.6} = \frac{0.87}{0.00439 \times 1.29} (\log 42 - \log 5) = 138.6$$

Having determined the coefficients E_{Cl} and E_{Br} we can easily calculate the amount of light transmitted through one or the other component separately. But for our purposes it is important to know the amount of light transmitted through both components at the same time, when they are either in a double filter or mixed. The mathematical relations in this case will be somewhat different, and I will now discuss these relations, taking first the case of a double light-filter, and then the more general case when we have in the filter an absorbing mixture of n components.

Let us imagine two light-filters, one with Cl, the other with Br. Let the concentrations be C_{Cl} and C_{Br}, thickness of layer X_{Cl} and X_{Br}. Let the intensity of the ray entering the first filter be I_o, the intensity of ray emerging from Cl filter be I_{Cl}, from Br filter be I_{Br}, and finally the intensity of ray passed through both filters be $I_{Cl + Br}$. The coefficients of absorption are E_{Cl} and E_{Br}.

I_o and I_{Cl} are connected by the equation

$$I_{Cl} = I_o .10^{-E_{Cl} C_{Cl} X_{Cl}}. \qquad (7)$$

Having passed the Cl filter the light will enter the Br filter with the intensity I_{Cl} and will emerge with the intensity $I_{Cl + Br}$.

$$I_{Cl + Br} = I_{Cl} .10^{-E_{Br} C_{Br} X_{Br}} \qquad (8)$$

Substituting in this equation the value for I_{Cl} from (7), we have

$$I_{Cl + Br} = I_o .10^{-(E_{Cl} C_{Cl} X_{Cl} + E_{Br} C_{Br} X_{Br})}. \qquad (9)$$

Denoting the total coefficient of absorption as E and

corresponding to it imaginary concentration and thickness of layer as C_o and X_o, we can write

$$I_{Cl + Br} = I_o \cdot 10^{-EC_o X_o} \tag{10}$$

or

$$EC_o X_o = E_{Cl} C_{Cl} X_{Cl} + E_{Br} C_{Br} X_{Br}. \tag{11}$$

If we want to calculate the total coefficient E from experimental data, e. g., from the intensity of image on the photographic plate, we must refer it to some real concentration and thickness of layer. It is natural to calculate E referring it to concentration and thickness of one of the components. If we take Br we get equation

$$EC_{Br} X_{Br} = E_{Br} C_{Br} X_{Br} + E_{Cl} C_{Cl} X_{Cl} \tag{12}$$

or

$$E = E_{Br} + E_{Cl} \cdot \frac{C_{Cl} X_{Cl}}{C_{Br} X_{Br}}. \tag{13}$$

Let us consider now a more general case, *viz.*, a light-filter containing an absorbing mixture of n components. In this case we cannot consider the absorption by each component separately, and must use differential equations.

Lambert gives the following equation correlating the intensity of light passing through some absorbing medium and the thickness of layer of the medium.

$$-\frac{dI}{dx} = \alpha I \tag{14}$$

This means that the change of intensity of the light is proportional to the intensity of light at a given depth of the layer. The coefficient, α, is characteristic for the substance through which the light passes. If we have n substances the process of absorption consists of n processes each proportional to the entire amount of light at a given depth of the layer. Let the proportionality coefficients for these components be $\alpha_1, \alpha_2, \alpha_3 \ldots \alpha_n$. Then we get the following equation:

$$-\frac{dI}{dx} = \alpha_1 I + \alpha_2 I + \alpha_3 I + \ldots\ldots\ldots \alpha_n I \tag{15}$$

or

$$\frac{dI}{dx} = (\alpha_1 + \alpha_2 + \alpha_3 + \ldots\ldots\ldots \alpha_n) I \tag{16}$$

hence

$$I_x = I_o e^{-x(\alpha_1 + \alpha_2 + \alpha_3 + \ldots\ldots\ldots \alpha_n)}. \tag{17}$$

Passing now from Lambert's formula to Beer's law, and substituting 10 instead of e, and k_1C_1, k_2C_2....k_nC_n instead of α_1, α_2....α_n, we get

$$I_{1,2,3....n} = I_0 \cdot 10^{-x(k_1C_1,\ k_2C_2.......k_nC_n)}. \qquad (18)$$

But this is the same expression that we deduced for the double light-filter. The only difference is that in this case the thickness of the layer x being the same for all components is outside the parenthesis. Therefore, if we determine the total coefficient of the mixture of Cl and Br on the basis of Br concentration, we get

$$E = E_{Br} + E_{Cl}\frac{C_{Cl}}{C_{Br}} \qquad (19)$$

where x is eliminated.

The value E—as previously mentioned—has no definite physical meaning since it is referred to arbitrary C and X, and changes with change of the ratio $\frac{C_{Cl}X_{Cl}}{C_{Br}X_{Br}}$ for double filter or $\frac{C_{Cl}}{C_{Br}}$ for mixture of Cl and Br. But this expression is important from the theoretical point of view, as it has the same form both for a double filter and for a mixture. By means of these formulae we can verify experimentally whether the components change chemically on being mixed, *i. e.*, whether the character of absorption remains the same in a mixture, as in a double filter.

I verified the above formula experimentally on my light-filter, and came to the conclusion that a mixture of dry Cl and Br follows Beer's law exactly. The verification consisted in taking photographs through the double filter and the mixture, and determining E from photographs, referring it to concentration and thickness of layer of Br. E obtained from these determinations was compared with E calculated from the formulae. The agreement of both figures points out at the normal absorption of a mixture of Cl and Br. In Table III are given the results for five different wave-lengths.

There remains now a practical problem to calculate the percentage of light passing through mixtures of different con-

centrations of Cl and Br and choose from these mixtures several more suitable for our purposes.

TABLE III

A. Cl and Br in separated filters

$C_{Br} = 0.002402$ $X_{Br} = 0.61$ cm
$C_{Cl} = 0.02189$ $X_{Cl} = 0.68$ cm $t_o = 5$ seconds

λ	t_x in seconds	E from experiment	$E = E_{Br} + E_{Cl} \dfrac{C_{Cl} X_{Cl}}{C_{Br} X_{Br}}$
390.6	18	317.6	318.8
356.0	39	509.3	508.5
313.0	36	489.4	494.9
275.9	8	116.5	119.4
253.6	6	83.4	81.5

B. Mixture of Cl and Br

$C_{Br} = 0.004783$
$C_{Cl} = 0.02223$ $X = 1.25$ cm $t_o = 5$ seconds

λ	t_x in seconds	E from experiments	$E = E_{Br} + E_{Cl} \dfrac{C_{Cl}}{C_{Br}}$
390.6	225	224.5	223.8
356.0	530	274.5	276.5
313.0	500	271.1	265.5
275.9	159	68.1	71.9
253.6	130	56.25	57.18

This problem is solved very easily. From Equation (1) we have

$$\frac{I_x}{I_o} = 10^{-ECX}$$

and the percentage p is determined as

$$p = \frac{I_x}{I_o} \; 100 = 10^{2-ECX}.$$

If we have two absorbing substances, e. g., Cl and Br, we get, in case the substances are separated,

$$P_{Br} = \frac{I_{Br}}{I_o} \; 100 = 10^{2-E_{Br} C_{Br} X_{Br}} \qquad (20)$$

$$P_{Cl} = \frac{I_{Cl}}{I_o} \; 100 = 10^{2-E_{Cl} X_{Cl}}. \qquad (21)$$

For a mixture we have

$$P = \frac{I_{Br + Cl}}{I_o} \; 100 = 10^{2-x(\epsilon_{Cl} c_{Cl} + \epsilon_{Br} c_{Br})}. \tag{22}$$

A very simple relation exists between the values P, P_{Cl}, P_{Br}

$$\frac{I_{Cl + Br}}{I_o} = 10^{-x(\epsilon_{Cl} c_{Cl} + \epsilon_{Br} c_{Br})} = 10^{-\epsilon_{Cl} c_{Cl} x} \, 10^{-\epsilon_{Br} c_{Br} x} \tag{23}$$

but

$$10^{-\epsilon_{Cl} c_{Cl} x} = \frac{I_{Cl}}{I_o} \text{ and } 10^{-\epsilon_{Br} c_{Br} x} = \frac{I_{Br}}{I_o},$$

hence

$$\frac{I_{Cl + Br}}{I_o} = \frac{I_{Br}}{I_o} \cdot \frac{I_{Cl}}{I_o}. \tag{24}$$

Multiplying both sides of the equation by 100 we get

$$\frac{I_{Cl + Br}}{I_o} \cdot 100 = \frac{I_{Cl}}{I_o} \cdot \frac{I_{Br}}{I_o} \cdot 100. \tag{25}$$

Multiplying and dividing the right part of the equation (25) by 100 we get

$$\frac{I_{Cl + Br}}{I_o} \, 100 = \frac{\frac{I_{Cl}}{I_o} \, 100 \cdot \frac{I_{Br}}{I_o} \, 100}{100} \tag{26}$$

or

$$P = \frac{P_{Cl} \cdot P_{Br}}{100}. \tag{27}$$

In Table IV are given values for P_{Cl} and P_{Br} for different concentrations of Cl and Br for 12 more important lines of the spectrum of quartz lamp. The following concentrations of Cl and Br were used:

Cl		Br	
I	0.011	1	0.00105
II	0.022	2	0.0023
III	0.044	3	0.0046
IV	0.088	4	0.0092
V	0.176	5	0.0184

Using values for P_{Cl} and P_{Br} from Table IV, I calculated from Formula 27 the percentage of light transmitted through

TABLE IV

λ	P_{Cl} at the concentration of Cl				
	I	II	III	IV	V
579.0	81.9	67.2	44.9	20.2	4.1
546.0	5.9	73.8	54.5	29.7	8.8
435.9	68.4	46.8	20.1	4.8	0.2
404.8	50.0	25.5	6.5	0.4	0.002
365.0	38.2	14.6	2.1	0.05	0.0
313.0	33.2	11.0	1.2	0.02	0.0
302.0	44.5	20.0	4.0	0.2	0.0002
296.7	58.8	35.0	12.0	1.4	0.02
265.0	83.6	70.0	49.0	24.0	5.9
253.6	89.0	79.2	62.8	39.4	15.5
232.6	85.9	73.8	54.5	29.7	8.8
226.3	85.9	73.8	54.5	29.7	8.8

λ	P_{Br} at the concentration of Br				
579.0	95.9	91.2	83.1	69.0	47.7
546.0	91.4	82.2	67.6	45.7	20.9
435.9	63.3	36.8	13.5	1.8	0.03
404.8	67.6	42.4	17.9	3.2	0.1
365.0	78.5	58.9	34.7	12.0	1.4
313.0	85.9	71.6	51.3	26.3	6.9
302.0	88.0	75.5	57.0	32.5	10.6
296.7	89.3	78.0	60.8	36.9	13.7
265.0	92.2	83.9	70.5	49.7	24.7
253.6	91.7	82.6	68.3	46.6	21.8
232.6	91.4	82.2	67.6	45.7	20.9
226.3	90.9	81.2	65.8	43.3	18.8

nine different mixtures of Cl and Br, composed of the above given concentrations of Cl and Br. (See Table V.)

The mixture 3/III comes near to concentrations of Cl and Br at normal conditions of temperature (18°) and pressure (740 mm).

From Table V it is evident that the minimum of absorption lies in the region of visible spectrum up to 500 $\mu\mu$, and then in ultraviolet region between 250–240 $\mu\mu$. Studying the photochemical action of light one has to take into consideration also the distribution of energy among the spectrum

lines of a given source of light. I, therefore, calculated the distribution of light energy among ten main lines of mercury lamp, taking the entire energy of light passed through the filter as 100. Table VI shows this distribution for the three most favorable mixtures of Cl and Br.

TABLE V

Percentage of light transmitted through mixtures of Cl and Br composed as follows:

λ	I/IV	2/III	2/IV	3/III	3/V	4/II	4/IV	5/I	5/II
579.0	70.0	40.9	17.9	37.3	3.4	46.3	13.0	49.1	31.9
546.0	27.1	44.8	24.4	36.8	5.9	33.7	13.5	17.9	15.4
435.9	3.0	8.4	1.8	3.0	0.03	0.9	0.09	0.02	0.02
404.8	0.3	1.9	0.1	1.2	0.0	0.5	0.008	0.05	0.009
365.0	0.04	1.3	0.03	0.7	0.0	1.8	0.005	0.6	0.2
313.0	0.01	0.9	0.01	0.6	0.0	2.9	0.0	2.3	0.8
302.0	0.1	3.0	0.1	2.2	0.0001	6.4	0.05	4.7	2.1
296.7	0.4	9.3	1.1	7.2	0.02	12.8	0.5	8.0	4.7
265.0	22.4	24.2	20.3	34.7	4.1	34.9	12.1	20.7	17.3
253.6	36.0	51.3	28.0	42.9	10.6	36.9	18.4	19.4	17.2
232.6	27.1	44.8	24.4	36.8	5.9	33.7	13.5	18.0	15.4
226.3	26.9	44.1	24.0	35.8	5.8	31.9	12.8	19.0	13.9

TABLE VI

λ	Mixture I 3/III		Mixture II 3/V		Mixture III 5/I	
435.9	9.78		4.74		0.65	
404.8	2.08		0.0025		0.08	
365.0	1.59	16.47%	0.0	4.752%	2.91	16.02%
313.0	1.46		0.0		6.71	
302.0	1.46		0.0		5.67	
296.7	5.19		0.041		11.99	
265.0	7.01		4.77		8.85	
253.6	37.6	83.53%	58.81	95.248%	29.34	83.98%
232.6	25.8		24.78		27.07	
226.3	7.35		6.84		6.81	

The first five lines belong to the part of the spectrum we want to eliminate. The second five are in the region we want to make use of. The distribution of light energy between these

two groups is about the same for the three mixtures, while
the distribution among different
lines differs considerably. In
the mixture I there is a distinct
maximum in the region 250–232
$\mu\mu$, but on the other hand too
much energy is spent on the un-
desirable blue line 435.9 $\mu\mu$.
In the mixture II there is even
a more distinct maximum in the
region 250–240 $\mu\mu$, and the
energy of blue light is rather
small. The mixture III has
more even distribution in the
lower group of lines and the blue
light is almost entirely absorbed. The graphic picture of distri-
bution of light is given in Fig. 3.
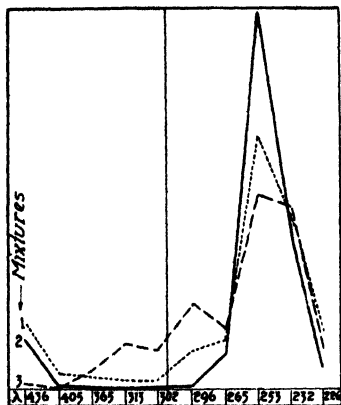
Fig. 3

Summary

1. Through qualitative study of spectrodiagrams a light-
filter was found which absorbs the region of spectrum between
500 and 300 $\mu\mu$. It consists of a mixture of gaseous Cl and Br.

2. Henri's photographic method for determination of the
coefficient of absorption in the invisible part of the spectrum
was developed and somewhat improved.

3. By means of Henri's method, absorption coefficients
of gaseous Cl and Br were determined for 43 lines of the quartz
lamp spectrum.

4. Mathematical treatment of the process of light absorp-
tion by mixtures of several components is given. By means
of formulae deduced, the question whether a mixture of Cl
and Br follows Beer's law was investigated experimentally.
The investigation gave positive results.

5. The light-filter found was subjected to quantitative
study. Mixtures of Cl and Br were found which could be
used for filtering off certain previously calculated regions of

spectrum. The region of transmitted light could be made as narrow as 250–240 $\mu\mu$.

In conclusion I wish to express my sincere gratitude to Professor J. S. Plotnikov for the use of his laboratory and his kind assistance.

Moscow, March 10, 1915

EQUILIBRIUM IN THE SYSTEM: CUPRIC CHLORIDE-PYRIDINE

BY J. HOWARD MATHEWS AND SAMUEL SPERO

Two compounds of cupric chloride with pyridine have been described previously, viz., $CuCl_2.2C_5H_5N$ by Lang,[1] and $2CuCl_2.3C_5H_5N$ by Lachowitz[2] and later by Schröder.[3] However, no detailed study of their solubility relations appears to have been made.

Materials Used.—A sample of Merck's pyridine was dried for several days over fused potassium hydroxide, then digested with potassium permanganate for eight hours, using a reflux condenser. It was then distilled off the permanganate and redistilled from barium oxide, the fraction coming over between 114° and 116° at 739.7 mm being reserved for use.

The cupric chloride was a Schuchardt preparation, and was recrystallized from water three times. The dried, finely pulverized salt was spread out in a thin layer and heated in an air-bath at 80° for three hours. Analysis showed it to be completely dehydrated. The anhydrous salt so prepared was kept in tightly stoppered bottles.

Method.—The solubility determinations were made with a modified[4] Meyerhoffer-Saunders[5] apparatus, which was immersed in a thermostat controlled (between 10° and 100°) by an ordinary toluene gas-regulator. Above 45° a layer of paraffine on the water aided greatly in the control of temperature, by prevention of evaporation. At 10° a stream of ice-water was passed through a lead coil immersed in the thermostat, to aid in maintaining a constant temperature. At 0° the solubility tube was surrounded with finely chipped

[1] Ber. deutsch. chem. Ges , 21, 1586 (1888).

[2] Monatsheft Chem., 10, 884 (1889).

[3] Zeit. anorg. Chem., 44, 1 (1905).

[4] Cf. Walton and Judd: Jour. Am. Chem. Soc., 33, 1039 (1911).

[5] Zeit. phys. Chem., 28, 464 (1899).

ice, which was kept thoroughly stirred. For the temperatures below 0°, mixtures of ice and salt and of ice and calcium chloride were used. As it is more difficult to maintain a constant temperature in this particular region, and because of the fact that temperature has a greater influence on the solubility of cupric chloride in this region than elsewhere, the determinations made at these lower temperatures are less certain than those made at temperatures above 0°. The location of the points on the curve seems to indicate that no serious error resulted from the slight temperature fluctuations experienced.

All temperatures above 0° were determined by means of a mercury thermometer graduated to 0.1° and capable of being read to 0.01°. For the temperatures below 0°, a toluene thermometer capable of being read to 0.1° was employed. Both thermometers were standardized by comparison with instruments, the corrections for which had been furnished by the United States Bureau of Standards.

Analysis of Samples.—A number of the customary methods for the determination of copper were tried. Of all those tested the following electrolytic method gave the most satisfactory results:

After weighing, the sample was washed into a porcelain casserole and evaporated to dryness on a water-bath. The residue was taken up with a few drops of dilute nitric acid, and the solution diluted to about 250° cc. This solution was brought to boiling and potassium hydroxide was added to precipitate the copper as oxide. After boiling for some time to coagulate the precipitate, the solution was filtered and the filtrate tested for copper. After rinsing once with distilled water, by decantation, the precipitate was dissolved in dilute nitric acid, and the resulting solution was poured through the filter into a weighed platinum dish. After washing the filter several times with hot water, about 2 cc of concentrated nitric acid were added to the solution, the volume of which was made up to about 150 cc, and the copper was deposited electrolytically using a rotating anode. Before siphoning off the liquid after

electrolysis, a few drops were always removed and tested for copper. Analyses made on our purified copper chloride by this method showed it to be accurate.

The data obtained are given in the following table, and are shown graphically by the accompanying curve. Tempera-

tures are plotted as abscissae and percentages of cupric chloride in the sample as ordinates.
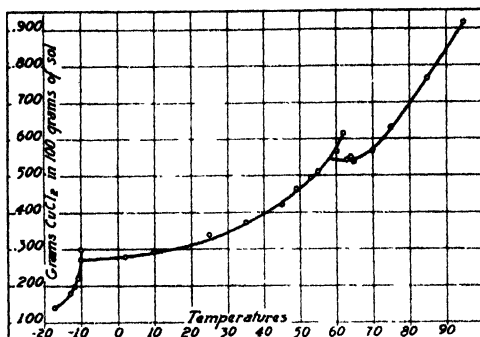
SOLUBILITY DATA

Temperature	Weight of sample	Weight of copper deposited	Percentage of cupric chloride in sample	Average percentage
A. Equilibrium between saturated solution and the solid $CuCl_2.6C_5H_5N$				
—17.3°	6.7175 gs	0.0047	0.148	
	7.0880	0.0044	0.131	0.140
—13.0	7.2788	0.0063	0.183	
	7.0602	0.0060	0.180	0.181
—12.1	6.5008	0.0058	0.189	
	7.0598	0.0067	0.201	0.195
—11.2	7.3572	0.0076	0.219	
	7.3855	0.0079	0.225	0.222
—10.0*	6.4598	0.0088	0.290	
	5.5190	0.0078	0.299	0.295

* Metastable points.

B. Equilibrium between saturated solution and the solid
$CuCl_2.2C_5H_5N$

—8.9	7.3958	0.0093	0.266	
	7.4690	0.0097	0.275	0.270
+2.0	6.7028	0.0089	0.281	
	3.3087	0.0042	0.269	0.275
10.00	7.7244	0.0105	0.288	
	5.9528	0.0083	0.295	0.293
	6.3746	0.0089	0.295	
25.00	6.1265	0.0100	0.345	
	4.5613	0.0076	0.352	0.348
35.00	6.6351	0.0117	0.373	
	5.8956	0.0109	0.391(?)	0.382
45.00	5.5593	0.0111	0.422	
	7 2783	0.0145	0.421	0.422
49.00	6.9589	0.0152	0.462	
	6.0618	0.0133	0.464	0.463
53.00	7.0590	0.0165	0.495	
	4.7097	0.0109	0.490	0.493
55.00	4.8899	0.0117	0.506	
	6.1453	0.0149	0.513	0.508
	5.7676	0.0138	0.506	
60.00*	5.3765	0.0142	0.559	
	4.2250	0.0114	0.571	0.565
61.00*	6.4458	0.0178	0.584	
	6.1363	0.0161	0.555	0.570
62.00*	4.6384	0.0132	0.602	
	5.3812	0.0160	0.629	0.616

C. Equilibrium between saturated solution and the solid
$2CuCl_2.3C_5H_5N$

63.00	6.1628	0.0159	0.546	
	5.0568	0.0129	0.540	0.543
64.00	5.8512	0.0153	0.553	
	5.4901	0.0142	0.547	0.550
65.00	4.6413	0.0118	0.538	
	5.4230	0.0136	0.531	0.535
70.00	5.8679	0.0160	0.577	
	6.3428	0.0167	0.557	0.567
75.00	5.8990	0.0176	0.631	
	5.6334	0.0168	0.631	0.631
85.00	5.2593	0.0195	0.784	
	6.7064	0.0235	0.741	0.763
95.00	6.2027	0.0270	0.921	
	5.7970	0.0250	0.912	0.917

* Metastable points.

The solid phase in contact with the saturated solution from —10° to about 58° was determined by analysis to be $CuCl_2.2C_5H_5N$. At about 58° there is a transition point, the solid phases $CuCl_2.2C_5H_5N$ and $2CuCl_2.3C_5H_5N$ being in equilibrium with the saturated solution. From 58° to 95° the solid phase in equilibrium with the saturated solution was found to be $2CuCl_2.3C_5H_5N$. Since both of these compounds are described in the literature no ultimate analysis was deemed necessary.

At —10° a second transition point was found. From this temperature to —17.3°, the lowest temperature at which solubility determinations were made, the solid $CuCl_2.6C_5H_5N$ was found to be the salt in equilibrium with the saturated solution. As this compound is stable only below —10° it was naturally difficult to obtain a satisfactory analysis of it on account of the danger of losing some of the combined pyridine in drying it. Analysis gave 9.95 percent copper, whereas theory requires 10.44 percent. There is little doubt but that the low result was due to imperfect drying of the crystals. This compound consists of minute, deep blue crystals, and has hitherto been unknown.

Summary

The equilibrium curves for cupric chloride–pyridine have been determined from —17.3° to 95.0°. The transition point between the two previously known compounds, $CuCl_2.2C_5H_5N$ and $2CuCl_2.3C_5H_5N$, was found to be at about 58°. At and below —10° a new phase appears, the composition of which appears to be $CuCl_2.6C_5H_5N$.

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LIQUID FILMS IN CAPILLARY TUBES

BY WILDER D. BANCROFT

If a liquid is adsorbed at a solid surface, it forms a liquid film there and we say that it wets the solid. If a liquid is not adsorbed by a solid, it does not wet the latter. There has been a good deal of question whether the liquid meets the wall at a definite angle, the contact angle, or whether the contact angle is zero. Lord Rayleigh[1] states definitely that in his opinion the contact angle is zero. This must be true if we consider that the liquid is adsorbed by the solid. The formation of a liquid film over the surface of a wetted solid accounts for the generally accepted fact that the rise of a liquid in a capillary tube is independent of the nature of the walls of the tube. This has always seemed a very improbable state of things and one that could only be justified by the fact that it was so. The whole thing becomes quite simple when we consider that the rising liquid does not come in contact with the walls of the capillary tube at all.[2] We are really dealing with the rise of a liquid in a liquid tube and it makes no difference what material is used to support the walls of the liquid tube. That this is the real explanation may be seen from the fact that concordant results are not obtained when a liquid is allowed to rise in a dry tube. To get good results it is important to immerse the tube in the liquid and then to raise it.

Bigelow and Hunter[3] claim that the nature of the walls does have an effect on the capillary rise. Their method of experimenting was very ingenious. After calling attention to the difficulty in working with opaque tubes, they point out that the height of a column of liquid in a capillary tube is determined by the radius of the tube at the meniscus, while the size or shape of the tube below the meniscus makes no difference. Accordingly, a tube of any convenient radius,

[1] Scientific Papers, 3, 393 (1902).

[2] Rayleigh: Ibid., 3, 421 (1902).

[3] Jour. Phys. Chem., 15, 367 (1911).

say 3 mm, may be closed at the top by a thin plate of any material, through which a small hole is bored. If the whole be immersed in a liquid and then gradually raised, a meniscus should form in this small hole and the whole tube should remain full of liquid until the height of the column is equal to that which would have been obtained with a long enough tube of the material of the plate, and of uniform bore the same size as the hole. When this point is reached, the meniscus should break away from the lower surface of the plate and the tube should empty. It is not even necessary to cement the thin plate to the glass tube. If the crack between the plate and the glass tube is less wide than the hole in the plate, it will fill with the liquid by capillary action and will not leak. It is an easy matter to grind off the top of the tube and to use flat plates so that the break always comes at the hole. The authors tabulated the highest and lowest values of the product of the radius of the hole into the height, and the data are given in Table I.

TABLE I
Plates of different substances with water
Temperature 20.5°-21°
Capillary rise (mm) in tube of 1 mm radius

Plate	High mm	Low mm	Average mm
Zinc	15.28	14.98	15.15
Copper	15.32	15.03	15.11
Nickel	15.12	14.89	15.00
Aluminum	15.04	14.63	14.78
Silver	14.89	14.61	14.75
Platinum	14.76	14.69	14.72
Glass	14.71	14.68	14.69
Celluloid	14.29	13.97	14.12
Beeswax	13.08	12.98	13.02
Paraffin	9.90	9.43	9.69

Though the values for the different metals are not far apart, yet the lowest value for zinc is larger than the highest value for silver and the highest value for glass is less than the lowest for nickel. Bigelow and Hunter say that "it both sur-

prised and interested us to find that with substances commonly
spoken of as 'not wetted,' namely, with celluloid, beeswax,
and paraffin, we could not only get ascensions but high and
regular ascensions. Our results with these substances agree
with each other as well as the results with plates of other
materials. We believe that our results are numerous enough,
and have been obtained with sufficient care, to justify the
statement that *water rises to different heights in capillary tubes
of different materials.*"

After showing that the capillary rise in the glass tubes
gives a value for the surface tension of water of 7.35 at 20.5°–
21.0°, whereas Volkmann found 7.40 at 20°, a satisfactory
agreement, they say: "Now if that is the value of the sur-
face tension of water at 20° what are we measuring when we
obtain our higher values with practically all the metals we have
tried, and when we obtain our lower values with celluloid,
beeswax, and paraffin? The surface tension of one liquid at
one temperature must be a constant, and since we obtain
different values, it cannot be surface tension which we are
measuring. It is possible that the contact angle between
water and glass is not zero, and that this angle is more nearly
zero between water and those substances with which we ob-
tained higher ascensions. This view is the more probable
as other methods for measuring the surface tension of water,
the drop method, the bubble method, the ripple method, all
give somewhat higher values than those obtained from the
ascensions of water in glass capillary tubes. But one has not
much more than stated the problem when he has demonstrated
that the angle is zero in some cases and greater than zero in
others. What interests us is, *why* is the angle different in
different cases, or as we prefer to state it, why is the ascen-
sion of a given liquid different in tubes of different materials?
This is a field in which but little, if any, direct experimental
evidence has thus far been obtained, owing to the lack of a
convenient experimental method.

"A liquid rises and is held at a definite height in a capil-
lary tube through the action of two forces, first, the cohesion

between the like particles of the liquid which, in the surface layer, is denoted by the phrase 'surface tension' and second, the adhesion between the liquid and the walls. The arrangement may be likened to a chain with two links, and when such a chain is strained to the breaking point it is the weaker link which gives way. So, here, whichever is the weaker, adhesion or cohesion, must break first. The cohesion of a given liquid at one temperature must be considered as constant, not varying. We find the phenomenon of 'breaking' at different strains, therefore, we must be measuring the force of adhesion. The force of cohesion must be the greater in all our experiments except those giving the highest results, and in those cases we have no sure means of knowing which of the two forces it is which gives way."

Bigelow and Hunter also made similar experiments with benzene and got similar results. The data are given in Table II.

TABLE II

Plates of different substances with benzene
Temperature 20.5° ± 0.2°
Capillary rise (mm) in tube of 1 mm radius

Plate	Rise	Plate	Rise (mm)
Silver	6 16	Copper	6 02
Nickel	6 11	Platinum	6.01
Aluminum	6.07	Glass	5.87

It should be noted that their method is not strictly comparable with the ordinary determination of the capillary rise. Under ordinary conditions the liquid rises along the walls of the tube whereas, in the experiments of Bigelow and Hunter, the meniscus is at the top of the so-called tube. This introduces a possible source of error. Then air may introduce another error. Of course, capillary rises are often measured in presence of air; but this is not strictly accurate and it is quite possible that the effect of air might vary to some extent with the nature of the tube because we are dealing with a displacement of liquid to some extent by air. The effect

of the air may very well be increased in the special apparatus used by Bigelow and Hunter with the meniscus at the hole in the plate. Of course, these possible errors may not amount to much in reality; but the conclusions of Bigelow and Hunter are so improbable, in view of what we know about adsorption, that we are justified in considering their experimental method as faulty until the contrary is proved.

On the assumption that the contact angle is zero, a thin film of liquid must rise to the top of the tube, irrespective of the height and diameter of the tube. This has been recognized explicitly by Lord Rayleigh.[1] "When liquid rises in a capillary tube open above, the more attenuated vapor at the upper level is in equilibrium with the concave surface, and the more dense vapor below is in equilibrium with the plane surface of the liquid. But the rise of liquid is not limited to the height of the meniscus. Above that point the walls of the tube are coated with a layer of fluid, of gradually diminishing thickness, less than the range of forces, and extending to an immense height. *At every point the layer of fluid must be in equilibrium with the vapor to be found at the same level.* The data scarcely exist for anything like a precise estimate of the effect to be expected; but the argument suffices to show that a solid body brought into contact with a vapor at a density which may be much below the so-called point of saturation will cover itself with a layer of fluid,[2] and that this layer may be retained in some degree even in what passes for a good vacuum. The fluid composing the layer, though denser than the surrounding atmosphere of vapor, cannot properly be described as either liquid or gaseous.

"In our atmosphere fresh surfaces, *e. g.*, of split mica or of mercury, attract to themselves at once a coating of moisture. In a few hours this is replaced, or supplemented, by a layer of grease, which gives rise to a large variety of curious phenomena. In the case of mica the fresh surface

[1] Scientific Papers, **3**, 523 (1902).

[2] This paper was published in Phil. Mag., (5) **33**, 209 (1892) and, therefore, antedates the paper by Cantor to which reference has been made

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conducts electricity, while an old surface, in which presumably the moisture has been replaced by grease, insulates well."

When the liquid does not wet the solid, mercury and glass for instance, the assumption of a zero contact angle leads to at least one awkward conclusion. The upper part of the meniscus is certainly not in contact with the glass and, therefore, none of the mercury is in contact with the glass. If we have a glass tube, infinitely long, closed at the bottom, and filled with mercury, we must conclude if we are going to be strictly logical that the column of mercury does not touch the glass at any point and that it stands alone, surrounded on all sides by a film of air, mercury vapor, or something which is not glass. Personally, I feel no desire to be so logical as that. It seems to me probable that at some point the force of gravity squeezes out all the vapor layer and the mercury does come in contact with the glass. This is the more certain because we know that the mercury sometimes tends to hang in a freshly made barometer and this could not happen if the mercury were not in contact with the glass.

Bigelow and Hunter are evidently not measuring the real capillary rise due to surface tension alone. They cannot be measuring the force of adhesion between the liquid and the walls because the liquid is not pulled off the wall, leaving the latter dry. They are not measuring the force of the cohesion of the water because the water slides over the wetted surface and is not torn from it. Besides, the values found are of quite different order from those obtained by Budgett[1] in his work on the tensile strength of liquid films.

"In recent years it has been found possible to polish plane surfaces of hardened steel to a degree of accuracy which had previously been approached only in the finest optical work, and to produce steel blocks in the form of end gauges which can be made to adhere or 'wring' together in combinations. Considerable interest has been aroused by the fact that these blocks will often cling together with such tenacity that a far greater force must be employed to separate them than

[1] Proc. Roy. Soc., **82A**, 25 (1912).

would be required if the adhesion were solely due to atmospheric pressure. It is proposed in this paper to examine the various causes which produce this adhesion: firstly, showing that by far the greater portion of the effect is due to the pressure of a liquid film between the faces of the steel; and, secondly, endeavoring to account for the force which can be resisted by such a film.

"The only previous experiments in this direction appear to be those carried out with Whitworth surface plates by Prof. Tyndall in 1875.[1] By wringing together two of these plates and suspending them in a vacuum he proved that the adherence between them was not caused solely by atmospheric pressure as had been previously supposed. According to Goodeve,[2] the conclusion at which Tyndall arrived was that the plates adhered by the molecular attraction of the bearing points brought into close contact by reason of the near approach to absolute truth of surface. Frequent references have been made to these experiments, and the conclusions of Tyndall appear to have been generally accepted.

"The author's curiosity was aroused by the fact that some steel gauges which he was constantly using in combinations did not always cling together with the same force. Frequently they refused to adhere to one another at all, while at other times considerable difficulty was experienced in getting them apart. On one occasion, when two blocks had been left wrung together for a long time, it was found necessary to hold one in a vice and hit the other sharply with a hammer in order to separate them. Subsequent examination showed that the faces had rusted together, which proved that some moisture must originally have been present between them. This led to the discovery that a minute film of condensed water vapor always formed upon the steel when the blocks were held with warm hands, and if care were taken to avoid this, and the faces were thoroughly cleaned with alcohol to remove grease, then all signs of adhesion vanished, and

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[1] Paper read at the Royal Institution by Prof. Tyndall, June 4 (1875).

[2] "The Elements of Mechanism," 272 (1897).

the blocks would fall apart under their own weight.   It soon·
became clear that the wringing effect was chiefly due to the
presence of a liquid film between the blocks, and it was de-
cided to make a series of experiments in order to examine—

    (1) The adhesive properties of various liquid films.

    (2) The effects of atmospheric pressure.

    (3) The force of attraction between the molecules of steel
in the two surfaces.

    "For these experiments a number of hardened steel
blocks were specially made in the form of cylinders 1 inch in
diameter and $^1/_2$ inch deep, having a central screwed hole
$^5/_{16}$ inch in diameter, the area of the faces being thus 0.7 square
inch.   These were specially polished with great care so that
their faces were true planes within the one-millionth of an
inch, the accuracy being optically tested by means of proof
glasses.

    "In testing the adhesive properties of various liquid films
the following procedure was adopted: The liquid under ex-
amination (with the exception of condensed water vapor)
was applied with a piece of clean linen to the faces of two
blocks which had previously been thoroughly washed with
alcohol and allowed to regain their normal temperature.   The
superfluous liquid was wiped off until only the barest film
remained, until, in fact, the ordinary observer would say that
the faces were perfectly dry.   In the case of condensed water
vapor, the blocks were held for an instant in the hands, or
near the breath, to allow a film of moisture to spread over the
steel, and were then quickly put together before evaporation
could take place.   The blocks were next wrung together with
a combined .sliding and twisting motion, which was found to
produce maximum results, and after a pair of screw handles
had been attached the force required to separate them nor-
mally was noted on a spring balance. . . .

    "No adhesion could be obtained with volatile liquids,
such as alcohol, benzine, and petrol; and viscous liquids,
such as glycerine, treacle, and glucose, produce very little
effect.   By rubbing the blocks on the hands after they have

been quite recently washed, very great adhesion takes place, and readings as high as 90 lbs. (over 8 atmospheres) were recorded. This must be due to traces of soap remaining on the hands, as only ordinary adhesion is obtained if all soap is carefully removed by rinsing the hands in clean water. Several attempts were made to apply soap films by other means, but these were unsuccessful.

"In order to determine what were the effects of atmospheric pressure arrangements were made by which, after being wrung together, the blocks could be separated in a vacuum. This was accomplished by means of a rod passing through an air-tight gland in the glass bell jar of a vacuum pump, and fixed to a spring balance within the jar. The lower end of the spring balance could be screwed through a universal joint into the upper block under test, the lower block being screwed to the plate of the pump. It is surprising to note that the force due to atmospheric pressure in no case exceeds 5 lbs., as, the area of the faces being 0.7 square inch, it might have been expected that this force would have approached 10.5 lbs. One would naturally suppose that such accurate surfaces with a grease-film between them, would be perfectly air-tight. It is evident, however, that air must have free access to a very large area of the faces, probably owing to the blocks being pulled apart or distorted slightly under the strain of the applied force, the film between them stretching before breakage occurs. It must be remembered that the volume required to fill the space between the faces, is exceedingly minute, and since the pull is increased very gradually a considerable time is allowed for the air to leak in or out. Thus with a fairly thick layer of Rangoon oil a difference of 6.5 lbs. was noted between the force of separation in air and *in vacuo*, the force due to the air in this case being 9.3 lbs. per square inch. This may be due to the air being more impeded by the thick oil, or to the faces being less distorted or separated, owing to a smaller force being required to cause breakage when a thick film is present. On the other hand, when the faces are perfectly clean and no film whatever

is present, the adhesion almost vanishes and the blocks will not support each other, although their weight is only 1.5 oz., showing that in this case the force due to atmospheric pressure is almost eliminated. For the same reason it is obvious that the force due to the attraction of the molecules of steel in the opposing faces is quite negligible in comparison with those which we are considering. . . .

"It seems probable that the results obtained by Tyndall in his experiments must be attributed to the presence of traces of grease or moisture on the surfaces of the plates rather than to molecular attraction, and we must conclude from our examination:

(1) That at least 75 percent of the adhesion is caused by the presence of a liquid film between the faces in contact.

(2) That no more than 25 percent is due to atmospheric pressure.

(3) That the adhesion practically vanishes when no film is present.

(4) That the attraction of the molecules of steel in one face by the molecules of steel in the opposite face is negligible."

Special experiments made Budgett conclude that at the moment of rupture the liquid covered only about one-tenth the face of the steel blocks. On this assumption and making the necessary deductions for atmospheric pressure and surface tension, he obtained the final data[1] given in Table III.

"These figures for the ultimate breaking strain of liquids are far higher than those previously obtained by other methods, probably owing to the fact that no air bubbles of any magnitude can possibly be present in the film, and the action of wringing the blocks together must bring the liquid into very intimate contact with the steel. It does not appear to be likely that results of this magnitude could ever be obtained with larger volumes of the liquids, and, in fact, if the thickness of the film is increased the pull required to cause separation rapidly diminishes. Thus if the blocks, when cold, are held by a person having very warm damp hands, an excess of the

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[1] Budgett: Proc. Roy. Soc., **86A,** 34 (1911).

moisture is deposited upon the steel, and it is difficult to obtain any wringing effect until the blocks have warmed up and some of the liquid has evaporated.

"It appears that there is a limit to which the thickness of the film can be reduced, and when this is reached the liquid will seize to the steel. The sliding and twisting of the blocks tends to further reduce the thickness by spreading the liquid, and this action is strongly resisted by the film, considerable force being necessary to move the blocks over one another. Soft metals will not stand the strains put upon them in this manner by the films between them, and the pieces may actually be dragged out of their polished surfaces. This is also very noticeable in glass and it is essential that optical proof planes should be perfectly free from grease before use, as otherwise they will be ruined. During the manufacture of lenses and proof glasses the faces are always cleaned with spirit of benzine before being put together, but this precaution appears to be taken more as a matter of traditional routine than owing to the knowledge of why it is necessary.

"As a result of our examination, we are led to the following conclusions:

1. Breakage occurs in the liquid itself, and not between the liquid and the steel.

2. Only 4 percent of the force required to rupture the film is due to the surface tension.

3. The remaining 96 percent must be necessary to overcome the molecular cohesion of the liquids.

4. The tensile strength of water may, under special conditions, amount to nearly 60 atmospheres."

It seems to me very likely that Bigelow and Hunter have studied, without knowing it, a phenomenon analogous to the breaking up of a liquid film into drops when it reaches certain thickness.

The spreading of one liquid over another is usually considered to depend on the relative surface tensions. If oil is dropped on water, it is assumed that we have a water-air surface, a water-oil surface and an oil-air surface. If the

surface tension water-air is greater than the sum of the surface
tensions oil-water and oil-air, the drop of oil spreads out over
the surface of the water.   If the water-air surface tension is
less than the sum of the other two the oil will draw up into
a globule.   While this may be a perfectly correct way of looking
at things, it is not a useful one because most cases where we
get globules of one liquid on another do not come under the
rule.[1]

    "How then is it possible that we should get a lens-shaped
mass of oil, as we often do, floating upon the surface of the
water?   Seeing that the general tendency of oil is to spread
over the surface of the water, why does it not do so in this
case?   The answer is that it has already spread, and that this
surface is not really a pure water surface at all, but one con-
taminated with oil.   It is in fact only after such contamina-
tion that an equilibrium of this kind is possible.   The volume
of oil necessary to contaminate the surface of the water is
very small; but I want to emphasize the point that, so far as
we know, the equilibrium of the three surfaces in contact
with one another, is not possible under any other conditions.
That is a fact not generally recognized.   In many books you
will find descriptions of these bodies in contact, and a state-
ment of the law of the angles at which they meet; that the sides
of a triangle, drawn parallel to the three intersecting surfaces,
must in be proportion to the three tensions.   No such equi-
librium, and no. such triangle is possible if the materials are
pure; when it occurs, it can only be due to the contamination
of one of the surfaces.   These very thin films, which spread
on water, and, with less freedom, on solids also, are of extreme
tenuity; and their existence, alongside of the lens, proves
that the water prefers the thin film of oil to one of greater
thickness.   If the oil were spread out thickly, it would tend
to gather itself back into drops, leaving over the surface of
the water a film of less thickness than the molecular range."

    "By means of the potential we may prove, independently
of the idea of surface tension, that three fluids cannot rest in

[1] Rayleigh: Scientific Papers, 3, 354, 413, 416 (1902).

contact. Along the surface of contact of any two fluids the potential must be a constant. Otherwise, there would be a tendency to circulation round a circuit of which the principal parts are close and parallel to the surface, but on opposite sides. For in the limit the variation of potential will be equal and opposite in the two parts of the circuit, and the resulting forces at corresponding points, being proportional also to the densities, will not balance. It is thus necessary to equilibrium that there be no force at any point; that is, that the potential be constant along the whole interface. It follows from this that if three fluids can rest in contact, the potential must have the same constant value on all the three intersecting interfaces. But this is clearly impossible, the potential on each being proportional to the sum of the densities of the two contiguous fluids, as we see by considering places sufficiently removed from the point of intersection."

The simplest way to look at the matter is to consider the adsorption. If oil is adsorbed by water, it wets the water and spreads over the surface. Now the adsorbed layer may be very thin, not over 2 $\mu\mu$. At greater thicknesses there is nothing to prevent the oil tearing loose from the oiled surface of the water and drawing up into drops under the influence of surface tension. This actually happens and has struck people as quite extraordinary.[1]

"When oil spreads upon water, the layer formed is excessively thin, about two millionths of a millimeter. If the layer be at first thicker, it exhibits instability, becoming perforated with holes. These gradually enlarge, until at last, after a series of curious transformations, the superfluous oil is collected in small lenses. It would seem, therefore, that the energy is less when the water is covered by a very thin layer of oil, than when the layer is thicker. Phenomena of this kind present many complications, for which various causes may be suggested, such as solubility, volatility, and—perhaps more important still—chemical heterogeneity. It is at pres-

[1] Rayleigh: Scientific Papers, **3**, 424 (1902).

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ent, I think, premature to draw definite physical conclusions; but we may at least consider what is implied in the preference for a thin as compared with a thicker film. We begin with a thin layer of oil on water and an independent thick layer of oil. In the second stage the thick layer is split in two, also thick in comparison with the range of the cohesive forces, and the two parts are separated. In the third stage one of the component layers is brought down until it coalesces with the thin layer of water. The last state differs from the first by the substitution of a thick film of oil for a thin one in contact with the water, and we have to consider the work spent or gained in producing change. If, as observation suggests, the last state has more energy than the first, it follows that more work is spent in splitting the thick layer of oil than is gained in the approach of a thick layer to the already oiled water. At some distances, therefore, and those not the smallest oil must be more attracted (or less repelled) by oil than by water."

This last paragraph is not very helpful and one has the feeling that Lord Rayleigh was a bit puzzled over the phenomenon. The whole matter is really quite simple. The first portion of oil spreads over the water because it is adsorbed and held by the water. The second portion of oil flows out over the oiled surface, but is instable because the same mass of oil would have a lesser surface if present in drops and still more so if present in a single drop. The excess oil, therefore, draws up into one or more drops depending on conditions, thereby leaving bare oiled surfaces. As Rayleigh puts it, one might think that the formation of holes in the film of oil was the primary phenomenon and the occurrence of drops or lenses a result of this; but that is not right. The film starts to break into drops and the holes are the result of that. The several drops will coalesce into one large one if brought in contact. If more oil is added the drops become larger and finally form so large a drop that under the influence of gravity, it covers the whole surface of the water and becomes a liquid layer of free oil. From this way of looking at it, we see that

the phenomenon must be general and so it is. Budgett[1] found that it was quite impossible to get a thin continuous film of kerosene or water on the surface of steel blocks. Microscopic examination showed that the applied films were not continuous membranes but that the liquid collected into small drops. This is undoubtedly exactly like Rayleigh's experiment. On the surface of the wetted steel the kerosene or water gathered in small drops. With different liquids we should expect to find the drops first forming when the films reached different thicknesses. This has been noted by Hardy.[2]

"When some ricinolic acid (Kahlbaum) is placed upon a clean surface of water the quantity added first spreads with great rapidity, but when the film is somewhere about 40 $\mu\mu$ thick, any further quantity added refuses to spread, but remains permanently gathered into a lens. When more acid is added to the lens it enlarges until the whole surface is covered with a layer of the oil which has been forced over it by gravity. Clearly, therefore, whereas the first added oil spreads because it lowers the tension, the sign of the effect changes at a certain stage in the thickening of the oil layer, further thickening increasing the tension. The spreading of the oil is, therefore, resisted, and a lens is formed. With some substances (olive oil, cymene, heavy oil), before the stage is reached at which a drop refuses to spread, small lenses, just visible to the naked eye, appear dotted all over the surface. In the case of cymene these tiny lenses are just visible when the oil film is of an average thickness of 100 $\mu\mu$, calculated on the assumption that its density is that of cymene in mass. The phenomenon can be followed in detail by adding successive drops of heavy oil[3] at the same spot. The result is a patch which is bounded by rings. Each drop allows the one last added to contract to a ring. The rings are of the same breadth when the drops are of equal size. The outermost ring of all—very visible when heavy oil is used—is the con-

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[1] Proc. Roy. Soc., **86A,** 30 (1911).

[2] Ibid., **86A,** 612 (1912).

[3] Distilled from Price's Motorine A.

tracted field of contamination on the surface before the oil is added. The color of the rings changes slowly. A drop of heavy oil spreads first to a patch of superb blue, then changes to purple with a defined yellow edge, 1 mm wide, the patch being (say) 5 cm across. The patch, up to now uniform, begins to become mottled, the red gives way to a beautiful patch of peacock-green, steel-blue, and bronze-yellow, the various colors being marked off sharply from one another even under considerable magnification. In the center of each blue patch, which in an undisturbed surface is accurately circular, is a small lens of oil, appearing as a point only to the naked eye.

"The mode of formation of these lenses is clear. Each is a droplet of oil condensed about some nucleus, for the most part solid, much more rarely a tiny bubble of gas. They appear on a surface of distilled water greased with the heavy oil when the average thickness of the film is approximately 200 $\mu\mu$. The surface, except at first, is therefore highly complex—colored areas and lenses being in tensile equilibrium. In these cases when the general surface is nearly saturated with oil, that is, when the minimum of surface energy is nearly reached, condensation occurs on any nuclei which may be present. The ultimate relation is the same as that found for ricinolic acid, or, indeed, for all the substances experimented with (olive oil, castor oil, croton oil, ricinoleic acid, benzyl cyanide, heavy oil, cymene and benzene); a uniform sheet of a third fluid in mass can only be inserted between the fluids, air and water, by the operation of an external force, namely, gravity."

In an appendix to the same paper, Hardy[1] says that "after the foregoing paper was completed, certain new facts came to light which make it possible to extend and confirm the conclusions arrived at. As will be remembered, a suspicion was expressed that the effect of the oil called 'heavy oil' upon the tension of water might be due to the presence in it of some active impurity. I wrote to Messrs. Price Patent Candle Co., asking them for information as to the chemical constitution of

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[1] Proc. Roy. Soc., **86A**, 632 (1912).

the oil 'Motorine A,' and especially whether the distillate I employed under the name 'heavy oil' might be taken to be composed entirely of paraffins. I did so because, as the simple paraffins are more stable than benzene, the chemical theory of the tension of composite surfaces demanded that the effect of paraffins upon the tension of water should be even less than that of pure benzene. The courteous letter which I received from Messrs. Price informed me that the Motorine A contains glycerides, which would account for its activity; further, that my distillate also might contain glycerides, that is esters, or products of the decomposition of glycerides. Messrs. Price sent to me a sample of a paraffin oil about as heavy as Motorine A, and about the same time I came, by accident, across another sample of an oil containing paraffins. These oils I will call B and C, respectively. Both of them refuse completely to spread upon pure water. The statement is founded upon the most rigorous tests I could devise. One experiment was as follows: The trough and blades were scrubbed with strong caustic potash, and left in running tap-water for one hour. The trough was then rinsed out with water freshly distilled in a silver still, filled with water, and the surface scraped at intervals for an hour. It was now not possible to detect any contraction of surface by the move-ment of motes. Carefully cleaned blades were inserted, and the tension found to be constant when the surface was con-tracted as much as possible. The barriers were placed at the extreme end of the trough. A very few grains of lyco-podium were then dusted on to one spot—very few in order to avoid risk of contamination. While the position of a particular cluster of grains was being observed along a fixed line of sight a small drop of oil B was placed on the surface 1 cm distant from the cluster. The cluster did not move at all, and the tension did not vary. A tiny drop of oil C was then placed 2 mm away from the cluster, again with no result. Each drop floated on the surface as a tiny lens. The barriers were now moved, and the surface contracted as much as possible, with no effect upon the tension. In contracting the

surface it was noticed that the lenses of oil did not move until they were impelled forward by the upward slope of the surface to the barriers. That is to say, the surface was so pure as to be 'non-contractile.' They were driven in this way right up to the blades. Both barriers were now lifted out, without any sign of expansion of a 'skin,' and placed touching one another in the middle of the length of the trough. They were then moved rapidly apart to each end, and on to the fresh surface so formed a few grains of lycopodium were placed, and oil drops beside them, all as rapidly as possible. The oil did not spread at all...

"The statement, so commonly made, that a drop of one fluid refuses to spread on the surface of another only when the latter is contaminated by a film of impurity is remarkably far from the truth unless the contamination in question be the air—an interpretation not usually included in the statement. I have found lenses of oil C on pure water unchanged after 24 hours, the edge still being tucked in. The lens, however, flattens at once if the clean water surface be *very* slightly oiled with an active substance such as castor oil......An instance of the fact that spreading is made possible, not prevented by a film of impurity, which must not be too thick, is furnished by oil B, which spreads slowly on tap-water but refuses to spread if the surface has been first thoroughly scraped."

If an oil is adsorbed by water, there is theoretically a film of air between the water and the drop of oil. It seems improbable that this air film can continue to exist when a thick layer of oil is present and yet, if not, there must be some point under some conditions when surfaces of oil, water, and air coexist. It seems probable that Rayleigh's conclusion, that such a state of things cannot exist, holds only when the effect of gravity is ignored. With increasing amount of oil there probably comes a time when the air film is squeezed out entirely.

The general conclusions of this paper are:

1. The rise of a liquid in a capillary tube is independent

of the nature of the walls, provided the liquid wets the walls.

2. The method of Bigelow and Hunter does not give the true capillary rise because the upper part of the tube is missing.

3. The method of Bigelow and Hunter does not give a measure of the adhesion of the liquid to the wall of the tube because the liquid is not removed from the wall.

4. It is probable that the results obtained by Bigelow and Hunter depend on the conditions under which air displaces a liquid from a wetted surface.

Cornell University

THE DISCHARGE POTENTIAL OF IONS ON HEATED ELECTRODES. I

BY JNANENDRA ·CHANDRA GHOSH

In a previous paper, it has been shown how the discharge potential of ions is considerably reduced when an alternating current is allowed to play between the electrodes.[1] In this communication, the variation of the discharge potential of ions with the variation in the temperature of the electrode will be described.

The temperature-coefficient of the electrode-potentials of several metals was first determined by Bouty[2] and later by Croustschoff and Sitnikoff[3] and Gockel.[4] The method consisted in measuring the potential difference between the electrodes of a cell, made up of two parts, which except for temperature are identical, e. g.:

$$\underset{\text{Hot}}{\underline{\text{Ag} \mid \text{AgNO}_3 \text{ Sol.}}} \cdots \underset{\text{Cold}}{\underline{\text{AgNO}_3 \text{ Sol.} \mid \text{Ag}}}$$
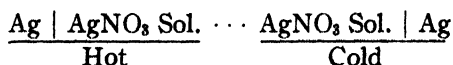
This method is, however, somewhat uncertain because the liquid potential at the junction of the hot and cold electrolyte cannot be ascertained. Again, the temperature coefficient of discharge potential at irreversible junctions yet remains to be determined.

To remove the difficulty caused by the indefiniteness of the liquid potential noted above, and to determine at various temperatures the discharge potentials of ions like SO_4'', NO_3', etc., where the phenomenon of overvoltage complicates the mechanism of ionic discharge, the following method was devised:

Experimental Procedure.—A single piece of thin platinum wire is sealed into three glass tubes, A, B and C, as shown in

[1] Jour. Am. Chem. Soc., **37,** 734 (1915).
[2] Jour. Phys., 8, 289, 341 (1879); **9,** 306 (1880).
[3] Comptes rendus, **108,** 937 (1889).
[4] Wied. Ann., **24,** 634 (1885).

Fig. 1, the length of the wire between A and B being equal to that between B and C. The wire is immersed in a dilute salt solution, and its temperature is raised by means of a variable electric current passing through the points A and C. On this wire is discharged the anion of the salt by another electric current passing through the circuit B E E' X.
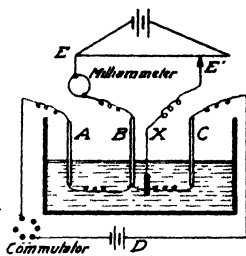
Fig. 1

Determination of the Temperature of the Wire.—It is obvious that the temperature of the wire will be higher, the greater the strength of the current passing through it. The heat evolved is C^2Rt/J, where C is the strength of the current, R the resistance of the wire, t the time, and J the mechanical equivalent of heat. When a thermal equilibrium is established

$$\frac{C^2Rt}{J} = KTt$$

where T is the difference in temperature between the wire and the solution and K is the rate at which heat is conducted away when the temperature difference is unity. Of course, this equation holds good only on the assumption that there is a thin film of constant thickness surrounding the wire, to which the variation in temperature is restricted. T can be determined experimentally by determining the variation of the resistance of the platinum wire, with varying current. This is easily done by putting in a standard coil of manganin wire immersed in an oil-bath in series with the platinum wire, and determining the potential differences between the ends of the coil and between those of the wire, when a definite current is passing. $C = P/R = P'/R'$, where P and P' are the potential differences at the ends of the coil and wire, respectively, and R, the resistance of the manganin coil. If P, P' and R are known, R', the resistance of the wire at various current strengths, can be calculated. We can now apply the formula

$$R' = R_0(1 + 0.00367t)$$

and since R_0, the resistance of the platinum wire, when the

current passing through is negligibly small, can be determined experimentally by the Wheatstone Bridge method, T can be calculated.

Fig. 2 shows how the resistance of the platinum wire, when immersed in pure water, varies when the current passing through is increased. Fig. 3 gives the calculated values of
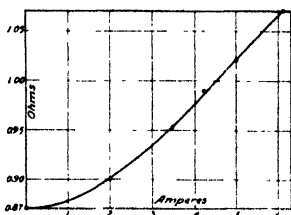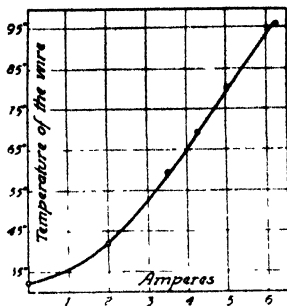
Fig. 2   Fig. 3

the temperature of the wire at various current strengths. Applying the equation

$$K = C^2 R / J T$$

to the actual experimental data, we find that K is not constant but increases as T increases. This is due to the fact that bubbles of vapor appear on the surface of the wire as the temperature rises, and these carry away heat by convection. Indeed, the temperature of the platinum wire could not be raised much above 100°, for then the variation of the temperature of the wire with the current becomes extremely indefinite and often the wire melts at some point and snaps into two. When dilute solutions of electrolytes, *e. g.*, $N/25$ $CuSO_4$, $CuBr_2$, etc., are substituted for pure water, curves were obtained which were identical with the above within the limits of experimental error. The time taken for thermal equilibrium to be established, was less than a minute and, therefore, the discharge potential can be determined when the whole mass of solution is at room temperature, the variation of temperature being restricted to a thin film on the surface of the wire.

The chief defect inherent in this method is that part of the current passing through the points A and C may be carried by the ions in solution. The following sources of error may be present due to this fact:

(1) The resistance of the platinum wire cannot be actually determined.

(2) A subsidiary current may pass through B E E′ X because the fall in potential from A to B due to the current passing from A to C, may not be the same as from A to X; thus a current may pass along B E E′ X if B is at a higher potential than X.

(3) The conduction of part of the current by the electrolyte is necessarily accompanied by the discharge, of anions near the positive end of the wire, and of cations near the other end.

Now the first error may be made negligible if, as has been stated before, a very dilute solution of electrolyte be used. For the elimination of the second error, it is necessary to adjust the position of X in such a way that the points B and X may be equipotential. For this purpose, a commutator was inserted in the circuit D A C and a very sensitive milliammeter (reading up to $^1/_6$ of a milliampere) in the circuit B E E′ X. The point X was so arranged by trial that the current indicated by the milliammeter was the same, whatever be the direction of the current along A C. When this condition was satisfied, the fall in potential between A B was the same as that between A X, and, therefore, the current passing through B E E′ X was due only to the potential difference between the points E E′. The third error is eliminated if the point B where we measure the discharge potential of ions due to the current through B E E′ X, be at the middle of the platinum wire.

In the actual determination of the discharge potential of irreversible ions, it is convenient to determine, first of all, the resistance of the circuit B E E′ X. Now we have

$$C = \frac{P_{EE'} - (P_B + P_X)}{R}$$

where $P_{EE'}$ is the applied electromotive force and P_B, P_X the

discharge-potential at B and X, respectively. The polariza-
tion E. M. F.s at B and X for the given current C were sep-
arately determined with the help of a calomel normal elec-
trode and potentiometer. Now C and $P_{EE'}$ are known, and,
therefore, R is known. Since the electrode X is made of metals
like Cu or Zn, P_x is almost independent of the current strength.
Hence, for any other current C' we have

$$C = \frac{P_{EE'} - (P'_B + P_X)}{R}$$

and P'_B can, therefore, be easily calculated for any current C'.

Experimental Results.—Figs. 4-7 show the variation of
the discharge potentials of SO_4'', NO_3', Cl' and Br' ions,
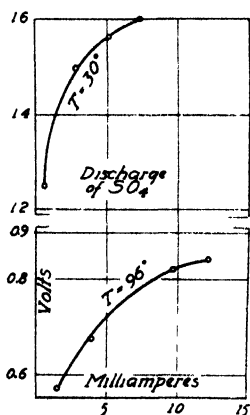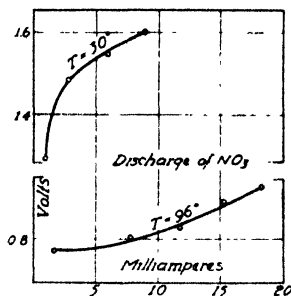
Fig. 4   Fig. 5

respectively, with the strength of the current. The potential
is given in volts, the electrode potential of a normal calomel
element being taken as zero. The electrolytes in these cases
were all pure salts of copper and the electrode X was also made
of a thin strip of pure copper. It will be observed that when
the temperature of the wire is 30° .C, the current potential
curve is almost vertical at first, and then tends to become
horizontal. The decomposition potential of SO_4'', NO_3', and
Cl' on the platinum wire at 30° are about 1.5, 1.45, and 1.6
volts, respectively. The marked difference between these

curves, and those obtained when the temperature of the wire is 96°, will be evident at once. Here the discharge potential has become almost independent of the current strength. So the effect of raising the temperature of the wire is to make the discharge of such ions as NO_3', Cl', or Br' resemble the discharge of reversible ions like $Cu^{..}$ or $Zn^{..}$. The decomposition
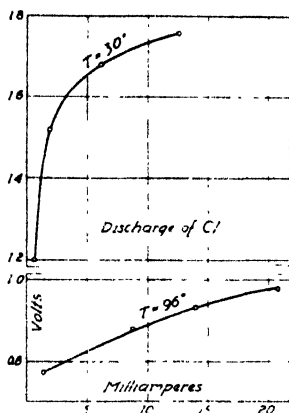
Fig. 6
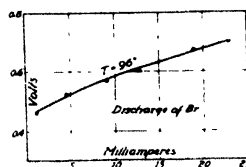
Fig. 7

potential at this temperature can easily be obtained by extrapolation. The voltages, when the current strength is zero, are 0.78, 0.75 and 0.45 for NO_3', Cl' and Br' ions, respectively; and these are the decomposition potentials. In the case of SO_4'' ion, the curve is not quite a straight line but shows a break at 0.8 volt.

	SO_4''	NO_3'	Cl'	Br'
Decomposition potential at 30°	1.5	1.45	1.6	—
Decomposition potential at 96°	0.78	0.75	0.45	0 8
Normal electrode potential at 25°	—	—	0 95	0.58

It is quite apparent that not only has the phenomenon of overvoltage disappeared at 96°, but that the decomposition potentials of Cl' and Br' ions are less than their respective normal electrode potentials.

Jnanendra Chandra Ghosh

Attempts were made to determine the discharge potentials of I′ ions under the above conditions by using the following electrolytic cell: Cd | CdI₂ | Pt wire (anode). The result obtained is given in Fig. 8. The curve is not at all similar to
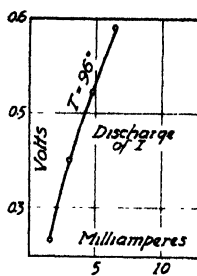
Fig. 8

those obtained with NO_3', Cl′, etc. This is, perhaps, due to the complex electrolytic dissociation of the salt CdI_2.

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NEW BOOKS

The Organism as a Whole. *By Jacques Loeb. 21 × 16 cm; pp. x + 379. New York: G. P. Putnam's Sons, 1916. Price: $2 50.*—"The book is dedicated to that group of free thinkers, including d'Alembert, Diderot, Holbach, and Voltaire, who first dared to follow the consequences of a mechanistic science —incomplete as it then was—to the rules of human conduct and who thereby laid the foundation of the spirit of tolerance, justice, and gentleness which was the hope of our civilization until it was buried under the wave of homicidal emotion which has swept through the world. Diderot was singled out, since to him the words of Lord Morley are devoted, which, however, are more or less characteristic of the whole group."

The headings of the chapters are. introductory remarks, the specific difference between living and dead matter and the question of the origin of life; the chemical basis of genus and species, specificity in fertilization; artificial parthenogenesis; determinism in the formation of an organism from an egg; regeneration; determination of sex, secondary sexual characters, and sexual impulses; Mendelian heredity and its mechanism; animal instincts and tropisms; the influence of environment; adaptation to environment, evolution; death and dissolution of the organism.

In the introductory chapter, the author says, p. 11: "Those familiar with the theories of evolution know the extensive rôle ascribed to the adaptations of organisms. The writer in 1889 called attention to the fact that reactions to light—*e. g.*, positive heliotropism—are found in organisms that never by any chance make use of them, and later that a great many organisms show definite instinctive reactions towards a galvanic current—galvanotropism—although no organism has ever had or ever will have a chance to be exposed to such a current except in laboratory experiments. This throws a different light upon the seemingly purposeful character of animal reactions Heliotropism depends primarily upon the presence of photosensitive substances in the eye or the epidermis of the organism, and these substances are inherited regardless of whether they are useful or not. It is only a metaphor to call reactions resulting from the presence of photosensitive substances 'adaptation.' In this book other examples are given which show that authors have too often spoken of adaptation to environment where the environment was not responsible for the phenomena. The blindness of cave animals and the resistance of certain marine animals to higher concentrations of sea water are such cases. Cuénot speaks of 'preadaptation' to express this relation. The fact is that the 'adaptations' often existed before the animal was exposed to surroundings where they were of use. This relieves us also of the necessity of postulating the existence of the inheritance of acquired characters, although it is quite possible that the future may furnish proof that such a mode of inheritance exists."

On p. 23 we read that. "The essential difference between living and non-living matter consists then in this: The living cell synthetizes its own complicated specific material from indifferent or non-specific simple compounds of the surrounding medium, while the crystal simply adds the molecules found in its supersaturated solution. This synthetic power of transforming small

'building stones' into the complicated compounds specific for each organism is the 'secret of life,' or rather one of the secrets of life.

"What clew have we in regard to the nature of this synthetic power? We know that the comparatively great velocity of chemical reactions in a living organism is due to the presence of enzymes (ferments) or to catalytic agencies in general. Some of these catalytic agencies are specific in the sense that a given catalyzer can accelerate the reaction of only one step in a complicated chemical reaction. . . . . . We shall see in the next chapter that each species seems to possess one or more proteins not found in any other but closely related species. Each organism develops from a tiny microscopic germ and grows by synthetizing the non-specific building stones (amino-acids) into the specific proteins of the series. This must be the work of the yet unknown synthetic enzymes or mechanisms. The elucidation of their character would seem one of the main problems of biology."

On p. 32 the author says: "The idea that the body cells are naturally immortal and die only if exposed to extreme injuries such as prolonged lack of oxygen or too high a temperature helps to make one problem more intelligible. The medical student, who for the first time realizes that life depends upon that one organ, the heart, doing its duty incessantly for the seventy years or so allotted to man, is amazed at the precariousness of our existence. It seems indeed uncanny that so delicate a mechanism should function so regularly for so many years. The mysticism connected with this and other phenomena of adaptation would disappear if we could be certain that all cells are really immortal and that the fact which demands an explanation is not the continued activity but the cessation of activity in death. Thus we see that the idea of the immortality of the body cell if it can be generalized may be destined to become one of the main supports for a complete physico-chemical analysis of life phenomena since it makes the durability of organisms intelligible."

The following passage, p. 108, is interesting though is seems distinctly unwise to talk about the osmotic pressure of a colloidal solution. "It is impossible to state at present whether the fertilization membrane is preformed in the fertilized egg and merely lifted off from the egg or whether its formation is due to the hardening of a colloidal substance separated from the emulsion (or excreted) and hardened in touch with sea water. But we can be sure of one thing, namely, that the liquid between egg and membrane contains some colloidal substance which determines the tension and spherical shape of the membrane. The membrane is obviously permeable not only to water but also to dissolved crystalloids, while it is impermeable to colloids. When we add some colloidal solution (*e. g* , white of egg, blood serum, or tannic acid) to the sea water containing fertilized eggs of *purpuratus*, the membrane collapses and lies close around the egg; while if the eggs are put back into sea water or a sugar solution the membrane soon assumes its spherical shape. This is intelligible on the assumption that in the process of membrane formation (or in the destruction of the emulsion in the cortical layer) a colloidal substance goes into solution which cannot diffuse into the sea water since the membrane is impermeable to the colloidal particles. The membrane is, however, permeable to the constituents of sea water or to sugar. Consequently sea water will diffuse into the space between membrane and egg until the tension of the membrane equals the osmotic pressure of

the colloid dissolved in the space between egg and the membrane. If we add enough colloid to the outside solution so that its osmotic pressure is higher than that of the colloidal solution inside the membrane the latter will collapse.

"It should also be stated that the unfertilized eggs of many marine animals are surrounded by a jelly (chorion) which is dissolved when the egg is fertilized. The writer has shown that the same chemical substances which will induce membrane formation and artificial parthenogenesis will, as a rule, also cause a swelling and liquefaction of the chorion."

Under animal instincts and tropisms, p. 279, we read that "Heliotropic reactions play a great rôle in the preservation of individuals as well as of species. In order to understand this rôle it must be stated that the photosensitive substances appear often only under certain conditions and that their effect is inhibited under other conditions. Thus among ants the winged males and females alone show positive heliotropism, while the wingless workers are free from this reaction. This positive heliotropism becomes violent at the time of the nuptial flight and this phenomenon itself seems to be a heliotropic phenomenon since it takes place in the direction of the light When the queen founds her nest she loses her wings and becomes negatively heliotropic again. Kellogg has shown that the nuptial flight of the bees is also a purely heliotropic phenomenon When a part of the hive remote from the entrance is illuminated the bees rush to the light and can thus be prevented from swarming These phenomena suggest that the presence of some substance secreted by the sex glands may cause the intensification of the heliotropism which leads to the nuptial flight."

On p. 300 we see how important it is to study cases in which the disturbing effect of secondary factors is eliminated as completely as possible "Although all normal human beings have about the same temperature, yet if the heartbeats of a large number of healthy human beings are measured the rate is found to vary enormously. Thus v. Korosy found among soldiers under the most favorable and most constant conditions of observations — the soldiers were examined early in the morning before rising—variations in the rate of heartbeat between 42 to 108. In view of this fact, those opposed to the idea that the organism as a whole obeys purely physico-chemical laws might find it preposterous to imagine that the rate of heart-beat could be used as a thermometer Yet if we observe the influence of temperature on the rate of the heart-beat of a large number of embryos of the fish *Fundulus*, while the embryos are still in the egg, we find that at the same temperature each heart beats at the same rate, the deviations being only slight and such as the fluctuating variations would demand This constancy is so great that the rate of heart-beat of these embryos could in fact be used as a rough thermometer. The influence of temperature upon the rate of heart-beat is completely reversible so that when we measure the rate for increasing as well as for decreasing temperature we get approximately the same values as the following table shows.

"Why does each embryo have the same rate of heart-beat at the same temperature in contradistinction to the enormous variability of the same rate in man? The answer is on account of the elimination of all secondary disturbing factors. In the embryo *Fundulus* the heart-beat is a function almost if not exclusively of two variables, the mass of enzymes for the chemical reactions underlying the heart-beat and the temperature. By inheritance the mass of

Temperature	Time Required for Nineteen Heart-beats in the Embryo of *Fundulus*
°C	Seconds
30	6.25
25	8.5
20	11.5
15	19.0
10	32.5
5	61.0
10	33.5
15	18.8
20	12.0
25	10.0
30	6.0

enzymes is approximately the same and in this way all the embryos beat at the same rate (within the limits of the fluctuating variation) at the same temperature. This identity exists, however, only as long as the embryo is relatively quiet in the egg. As soon as the embryo begins to move this equality disappears since the motion influences the heart-beat and the motility of different embryos differs.

"In man the number of disturbing factors is so great that no equality of the rate for the same temperature can be expected. Differences in emotions or the internal secretions following the emotions, differences in previous diseases and their after-effects, differences in metabolism, differences in the use of narcotics or drugs, and differences in activity are only some of the number of variables which enter."

Wilder D. Bancroft

Technology of Paint and Varnish. *By A. H. Sabin. Second revised edition. 23 × 16 cm; pp. x + 473. New York: John Wiley & Sons, Inc., 1917. Price: $3 50* —In the preface the author says: "In the twelve years which have passed since the first publication of this work, certain changes have come about, which seem to make a new edition desirable. The most important is the use of tung oil in varnish-making, which has entirely changed the character of cheap and medium-priced products. Varnishes containing it dry with a rapidity and hardness unknown before, which lessens the time needed for finishing work; and its remarkable water-resisting quality makes rosin-varnishes more durable and better in every way   But surfaces thus finished become hard and crack; the general appearance of furniture and of railway passenger coaches and medium-priced carriages of every sort throughout the country has grown worse rather than better during the last ten years."

The chapters are entitled: introductory; early history; origin of the name varnish; linseed oil; linoleum; manufacture of varnish; tung oil; japans and driers; rosin; spirit varnishes; pyroxylin varnishes; oil-paint and paints in japan; varnish or enamel paints; Chinese and Japanese lacquers; protection of metals

against corrosion; water-pipe coating; ship's-bottom paints; ship- and boat-painting; carriage-painting; house-painting; furniture-varnishing; conclusion.

This is an interesting and readable book; but it is apparently very difficult for an expert to realize what the layman wants to know, and most of that is omitted because the author supposed that everybody knew it. What resins are actually used in carriage-painting, just what is spar varnish, why does hot water play havoc with a dining table and what resin was or should have been used, what are some of the details in regard to baking-japans? While one might like to know the answers to these questions, one cannot complain, because the author says quite frankly that "apology is perhaps due the reader for the lack of a very coherent plan in this treatise. In part the contents of this book are those things which seem most interesting or important to the writer; in part they are things which long practical experience has shown to interest many other people. Things which many people will wish to know are left out, in many cases because of the limitations of the author's knowledge, but often because the book is already too large " To all the writer commends the amiable maxim of Erasmus that "a reader should sit down to a book as a polite diner does to a meal. The entertainer tries to satisfy all his guests, but if it should happen that something does not suit this or that person's taste they politely conceal their feelings and commend other dishes, that they may not distress their host."

One sees the author at his best in the following extract from the chapter on early history, p. 19.

"The foregoing formulae, which are selected from a great number known to the writer, give a fair idea of the knowledge of the art of varnish-making in the middle ages The conclusion I have reached from a careful study of the whole subject, as far as the records are accessible to me, is that the best varnish was made from amber, or rather from what was called amber, the term being made, as the records show (but which are not included here on account of lack of space), to include certain hard varnish resins from the East This varnish was made originally without spirits of turpentine or any other thinner, and in order to have it sufficiently liquid it was made with a large amount of oil, from twenty-five to fifty gallons of oil to the hundred pounds of resin (to put it in the terms of modern varnishes), well-cooked and slow-drying The oil was carefully refined, as will be described later, and probably was made drying with litharge and possibly with umber, but the painter expected to allow a long time for his work to dry, in some cases a year or more for the paint to dry before the final varnishing; and if haste was necessary, the use of an oven or other source of heat was the alternative There was practically no progress for eight hundred years, the varnish made by Theophilus being quite equal to that made in the eighteenth century, and when a really good varnish was desired recourse was had to this old formula, which was handed down from one generation of artisans to another. There were no varnish-makers in the modern sense until the nineteenth century, *i. e*, no established business of varnish-making, but every important manufacturing establishment had its own varnish-maker, who made up small quantities, but the more important apothecaries in the large cities sold, and in some cases made, varnish; sometimes "common liquid varnish," only which was made with sandarac or other cheaper resin, sometimes this and also amber varnish. But always small batches were made.

Near the end of the eighteenth century Tingry, the most noted varnish-maker of his time, warns his followers that six ounces of amber is as large a melt as is advisable. It will further be shown that varnish was known before the Christian era, and there can be no reasonable doubt that knowledge of the art was continuous from at least as early as 500 B. C., when those varnishes were made which still exist on the Egyptian mummy-cases already mentioned, down to the present time, and it seems likely that the formula of Theophilus may have been handed down from those early Egyptian workmen. This latter conclusion may strike the reader as an unsupported conjecture; and since the matter is one of interest to all those who care to know about the origin of the art, it is worth while to give some of the grounds which seem to support such a proposition.

"In the first place, nothing is so conservative as tradition in artisanship. We still wear the buttons on our coat sleeves which were used by our ancestors in the dark ages to fasten back their sleeves when they went into battle, and those on the backs of our coats with which they buttoned up their skirts to ride in the saddle. Hundreds of such instances are known to the student. Those who have not studied such things cannot imagine how persistent habits and methods of workmanship are. The fact that the process of Theophilus, which he put down as the old and approved one, continued for hundreds of years after his time and is still almost exactly practised, only with some additions and on a larger scale, a thousand years after it was known to the men who communicated it to him, is in reality a substantial reason for believing that it had then existed a long time. This is also strongly supported by the appearance of the Egyptian varnish. Too much stress cannot be laid on the fact that here we are not dealing with tradition or history, but with the real and actual thing. Here is the varnish, just as it was applied twenty-five hundred years ago. It is just as real as the mummy itself, and is just as absolute a proof that varnish was made in those days as the mummy is proof that people lived in those days. Here, I say, is the actual and real varnish. It was made with resin and oil It was smeared on, possibly with a spatula, but more likely with the fingers, certainly not put on with a brush nor in a thinly fluid condition. Such a varnish as Theophilus describes would look as that looks, and in all probability would last as that has endured." *Wilder D. Bancroft*

Laboratory Manual of General Chemistry. *By Arthur B. Lamb.* 27 × 21 *cm; pp. vi + 166 (+ 130 pages for notes). Cambridge: Harvard University Press, 1916. Price: $1 45.*—This is a special manual for those students who have had some chemistry at one of the better high schools. "Those students who have studied chemistry in the secondary school have already done a large share of the simple, important, and impressive experiments. The first freshness of their interest in, and wonder at, chemical phenomena has been lost. On the other hand, to trust that the average college student retains any clear conceptions regarding the abstract matter of his secondary school chemistry, which is so important as a basis for further study, is to court disappointment. Besides, as every experienced college teacher knows, the very familiarity of such students with parts of the subject frequently leads to over-confidence about the whole of it—with disastrous results. Flagging interest then, hazy ideas about the principles of chemistry, and over-confidence are the special difficulties of the problem.

"The requirements then to be met by a laboratory manual of this kind are by no means easy. The most essential are, first, that those important facts and principles which the student has already studied shall be reviewed in a way sufficiently novel not to bore him, nor to encourage him to over-confidence; second, that the student's chemical horizon shall be widened by the study of new and unfamiliar substances; and third, that further important generalizations upon which the superstructure of the science is based, shall be disclosed and made clear. To meet these requirements I have resorted to several expedients. For instance, to review the weight relationships of chemical reactions, I have devised a series of simple, quantitative experiments quite different from the ones usually performed in a strictly elementary course. A number of new experiments of a semi-quantitative nature have also been devised, illustrating such matters as the vapor pressure of solutions, reaction velocity, catalysis, the strength of oxidizing agents, etc."

Among the experiments are ones on ᵧautoxidation, velocity of chemical reactions, chemical equilibrium, electrical conductivity of solutions, ionic equilibria, hydrolysis, catalysis, over-voltage, solubility, boiling-points of solutions, chromous acetate and colloidal solutions. This is a very interesting set of experiments and makes one wonder what lectures go with them. It is quite certain that the author is right in saying that only an exceptional student can do all the sixty-seven experiments in thirty-three-hour periods and it seems rather remarkable that every student can be required to complete four-fifths of them. *Wilder D. Bancroft*

A Laboratory and Classroom Guide to Qualitative Chemical Analysis. *By George F White. 19 × 13 cm; pp. v + 171. New York: D. Van Nostrand Co., 1916. Price: $1.25* —In the preface the author says: "In compiling this book, the author has endeavored continually to bear in mind the fact that the main objective of a course in qualitative analysis is the attainment of a knowledge of the fundamental principles underlying the differential behavior of elements and compounds Ability to devise and execute schemes of analysis should be developed naturally. With this point of view, a study of reactions has been combined with methods of analysis, the latter being considered as practical applications of previously observed phenomena. It is considered that this book satisfies the need of a manual for students who have completed the usual college course in general chemistry. Such students have acquired some knowledge of the physical laws underlying chemical reactions and yet, in the author's experience, too often have only very indefinite conceptions of these laws. There are books at hand which present advanced theories in detail, and there are others which lay especial stress on analytical procedures and laboratory practice. Such texts are admirable for reference. This book is offered as a working manual which presents the essentials of both theory and practice, but which also suggests the possibilities for more extended study and experimentation.

"Emphasis has been laid in the first part of the course on the reversibility of reactions, equilibrium phenomena, and the laws governing the behavior of electrolytes, while many applications of these principles have been left to the student in his later work. The brief outline of the electrolytic dissociation theory presented, is meant to be supplemented by class-room questions and instruc-

tions; this is also true of the individual base-forming and acid-forming constituents, analytical procedures, etc.

"While much may be said for the progressive study of the base-forming constituents beginning with the alkalies, the silver-group metals have been first considered in order to co-ordinate the study of reactions with the scheme of analysis offered. The first year's work in general chemistry should have furnished the student sufficient knowledge of the alkali group and the general properties of the metals to enable him to appreciate the full significance of the reactions as carried out.

"The dimethyl-glyoxime test for nickel, and the nitroso-betanaphthol test for cobalt have been found in this laboratory to be particularly successful in the hands of the beginner. The cobalt test was successful, however, only after being modified in such a way that there is no possibility for the reagent to be precipitated."   *Wilder D. Bancroft*

Introduction to Inorganic Chemistry. *By Alexander Smith,   Third edition. 20 × 14 cm; pp. xiv + 925.   New York: The Century Co., 1917.   Price, $2 60.—* The first edition of this book was reviewed over ten years ago (**10**, 719) under the title "Introduction to General Inorganic Chemistry." The new edition has been modified somewhat and has been brought up to date, even the apparently varying atomic weight of lead being included, p. 54. Like other books by the same author, the book covers a marvelous amount of ground. It might be called a condensed treatise on introductory chemistry, inorganic chemistry, and physical chemistry. If the author can really teach the essential parts of this book to a freshman without a process of cramming which would be bad for the student's health and brain, then the general chemistry of other universities needs a very vigorous overhauling   Either the author has a positive genius for teaching—which is the general belief—or he is a very misguided enthusiast. It seems a pity that there is no way of deciding to general satisfaction whether Columbia has outstripped the other universities in the teaching of freshman chemistry or whether she is the victim of a colossal mistake. So far as the reviewer can see, there is no middle ground and one must line up on one side or the other if one has any opinion at all.   In any case this book can be considered as representing one ideal of what a beginner should be taught.

There are only a few casual statements which should be changed.   Bredig has shown pretty conclusively that the catalytic action of platinum on hydrogen peroxide is not a mechanical one, p. 318.   Willard Gibbs did not predict that a colloid would tend to reach a higher concentration in the surface layer than elsewhere in the liquid, p. 624.   He discussed the behavior of true solutions and he should not be held responsible for the fact that other people have misapplied his formula.   The reviewer does not sympathize at all with the author's attitude in regard to "nascent" hydrogen, p. 543.   It is really monatomic hydrogen of varying concentration.   This, however, is a matter on which a difference of opinion is permissible.   *Wilder D. Bancroft*

SEMIPERMEABLE MEMBRANES AND NEGATIVE ADSORPTION

BY WILDER D. BANCROFT

Mathieu[1] observed negative adsorption with a number of dilute solutions when adsorbed by porous plates, membranes, or capillary tubes. With normal solutions the concentrations in the capillary tubes were often only one-tenth that. The difference in concentration increases with decreasing radius of the capillary tube and Mathieu considers it quite possible that with very fine tubes water alone would be adsorbed, a conclusion which, as Mathieu himself points out, is of distinct importance for the theory of semipermeable membranes. If this conclusion is true and general, it accounts for the results of Bigelow[2] and of Bartell[3] on osmotic pressure. In the 1912 paper Bartell says: "The fact that some grades of porcelain act 'osmotically' was clearly demonstrated by Graham.[4] He made use of a porcelain cylinder of about 170 cc capacity, to which was attached an outlet tube calibrated in millimeters, for measuring the change of height of the solution. This apparatus was filled with the solution to be tested, then placed in a jar of distilled water, the temperature of which was held between 56° and 64° Fahr. Some of the results obtained are as follows: A solution containing 1 percent of Rochelle salt produced a rise in the column of 82 mm; phosphoric acid of the same strength gave 62 mm; sugar and other organic substances gave something less than 20 mm.

"Notwithstanding the fact that certain grades of porcelain do produce osmotic effects when tested, it is also true that most grades of porcelain do not produce apparent osmotic effects. The difference in the behavior of the porcelain con-

[1] Drude's Ann., **9**, 340 (1902).
[2] Jour. Am. Chem. Soc., **29**, 1576, 1675 (1907); **31**, 1194 (1909).
[3] Jour. Phys. Chem., **15**, 659 (1911); **16**, 318 (1912); Jour. Am. Chem. Soc., **36**, 646 (1914); **38**, 1029, 1036 (1916).
[4] Phil. Trans., **144**, 177 (1854).

sequently raises the following questions: What is characteristic of that porcelain which is capable of producing osmosis? Is the *composition* of the porcelain or the *internal structure* the principal factor, and, if the latter, is there any definite relation between the size of the pores in the porcelain and osmotic effects?" Microscopic examination of different samples of unglazed porcelain showed that those which produced the osmotic effects were those with the finest texture and therefore presumably those with the smallest pore diameters. It therefore seems reasonable to suppose that, if the size of the pores makes the difference, osmotic effects should be obtained from a plate, which alone will not show osmotic effects, provided its pores be sufficiently clogged with some insoluble material. In Table I are given the pore diameters, above which no osmotic pressure effect was obtained and the pressures at which 100–125 air-bubbles are forced through the diaphragm.

TABLE I

Pressure in kg/cm² necessary to force 100–125 air-bubbles through the diaphragm. Limiting pore diameter in microns at which osmotic effects occur

Diaphragm	Pressure kg/cm²	Pore diameter μ
Porcelain	7.0	0.422
Porcelain and sulphur	5.0	0.591
Porcelain and BaSO₄	4.0	0.738
Porcelain and PbCrO₄	3.8	0.777
Porcelain and PbSO₄	3.2	0.923
Porcelain and CuS	4.0	0.738
Porcelain and Cu₂Fe(CN)₆	3.2	0.923

"The border line between osmotic effect and no osmotic effect is not quite the same for the different membranes; however, the values are of the same order of magnitude and probably agree as closely as could be expected, for comparatively large errors are possible in determining the pressure at which 100–125 bubbles appear. Since these values are not the same, it cannot be stated definitely that the nature of the substance makes no difference; but they are so nearly the same that the

pore diameter seems to be one of the main factors in determining the appearance of osmotic phenomena. The success of finding within rather narrow limits a pore diameter which, if exceeded, unsuits the membrane for demonstrating osmotic effects does not exclude the following possibility. Perhaps it is only through the pores of molecular dimensions that pure water passes through to the solution while the solution as a whole is leaking outward through all the large pores. When the inflow equals the outflow, no change in level is observed; when the inflow slightly exceeds the outflow, a change in level is observed. Perhaps what was measured in this investigation was the pore diameter at which the 'leak' was just a little less than the osmotic effect." The general conclusion drawn by Bartell is that there is no osmotic effect when there are 100–125 pores, in the observed area of about 1.5 cm, w th diameters greater than 0.923 microns. "The border line between osmotic effect and no osmotic effect seems to be practically the same for membranes clogged with insoluble crystalline precipitates and for those clogged with the so-called 'semipermeable' precipitates."

In the chapter on Osmotic Phenomena Bigelow[1] says:

"By some the function of the membrane in osmotic phenomena is considered to be a subordinate question, because it can be demonstrated that the nature of the membrane, assuming perfect permeability, makes no difference. This demonstration runs as follows: Imagine a long tube divided into compartments by two diaphragms, perfectly semipermeable, but of such natures that the first is capable of 'generating' a higher osmotic pressure than the second. Imagine the chamber made by the diaphragm filled with a solution and the rest of the tube full of water. Water will pass in through both membranes until the pressure is the maximum the second can generate. It will continue to come in through the first but will then begin to pass out through the second. Since the membranes are not altered, and all solute is retained in the chamber, water will continue to flow in through the first and

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[1] Theoretical and Physical Chemistry, 218 (1912).

out through the second forever. We could insert a water wheel and make the current do work, thus realizing a perpetual motion machine, one to do work at no expense. Such a machine is impossible, therefore the two diaphragms cannot have the difference assumed for them. Therefore, the maximum osmotic pressure must be the same for all perfect membranes. This is entirely conclusive, being just as certain as the premise that a perpetual motion machine is impossible; but, like so much thermodynamic reasoning, it leaves us exactly where we started without adding one iota to the actual sum of our knowledge.

"As a matter of fact we seldom have to do with conditions wherein even approximately maximum osmotic pressures become evident, but we have to do constantly, whether we will or not, with what we may call traces of osmotic pressures, for the majority of our life processes are secretions by glands, and through membranes which permit the passage of this and hinder the passage of that. Unless the countless membranes in our bodies have their appropriate permeabilities, sickness and death ensue. Hence the majority are not satisfied to let the matter rest with a thermodynamic demonstration that the nature of the membrane makes no difference but will continue experimental investigations in the hope to find a cure for indigestion, rheumatism, and allied complaints.

"The earliest publications on osmosis considered the membranes as capillary structures, and many were the efforts to account for the endosmotic and exosmotic currents on the basis of the behavior of liquids in capillary tubes. One liquid adhering closely to the inner walls constituted a liquid tube moving in one direction while an interior core of the other moved in the opposite direction. These suggestions are not satisfactory as a statement of the cause of the observed effects.

"Then it was thought these capillary structures acted like sieves, permitting the passage of molecules of solvents because they were smaller than the holes, and preventing the passage of solute because its molecules were larger than the

holes. It has been brought forward against this theory that membranes are known which permit the passage of the large molecules of various alkaloids while holding back the smaller molecules of amido acids. It is here silently assumed that the size of the formula we write for a substance is a measure of the size of the individual molecule. This is rather hypothetical. The argument might be met on its own ground by the assumption that a very long carbon chain might worm its way through a hole so small a benzene ring could not enter.[1]

"Experiments of extraordinary interest were carried out by Lhermite.[2] In a test-tube he put some water, above this a thin layer of alcohol. In the course of a day or two the alcohol had passed through the oil to the water and there were but two layers in the tube, the solution of alcohol in water and the oil above it. He substituted turpentine for the oil with the same result. He separated a layer of chloroform from a layer of ethyl ether by a layer of water and the ether passed through to the chloroform. He tried eight different combinations. Of particular interest, as foreshadowing our present devices, is the following experiment of his. He put alcohol in a porous cup, immersed it in water and observed that the water passed in to the alcohol. He next filled the pores of the cup with castor oil, filled the cup with alcohol and immersed it in water as before. With this modification the alcohol passed outward to the water. As a result of these experiments he stated that substances which pass through membranes first dissolve in them. Many investigators at present entertain the opinion that membranes with which osmotic phenomena may be produced must be able to dissolve the substance which passes through. That this is not essential is proved by the fact that small excess pressures may be obtained with a cracked test-tube for a membrane.

[1] The writer in conjunction with F. E. Bartell has estimated the size of the capillary holes in the coarsest-grained porcelain with which small, but definite osmotic pressures may be obtained, and finds the diameters of these holes in the neighborhood of one thousand times the probable diameters of molecules. For details, see Jour. Am. Chem. Soc., **31**, 1194–1199 (1909).

[2] Ann. Chim. Phys. (3) **43**, 420–431 (1855).

Wilder D. Bancroft

"It is possible to look upon a liquid, or solution, as a capillary structure, for there must be space between the molecules else it would be continuous, infinitely divisible, and we should have to abandon our molecular theory."

Since a copper ferrocyanide membrane is distinctly colloidal, it is necessary to consider to what extent adsorption helps or hinders osmosis. This point has been discussed at length by Trouton.[1]

"The investigation of adsorption and absorption should throw light on osmosis, as in the first place the phenomenon occurs across a surface necessarily covered with an adsorption layer, and in the second place, as we shall see, the final condition is an equilibrium between the absorption of water by the solution and that by the membrane. The study of the conditions of absorption of water throughout the mass of the colloidal substance of which osmotic membranes are made is of much interest. Little work has been done on the subject as yet, but what little has been done is very promising.

"It is convenient to call the material of which a semipermeable membrane is made the semipermeable medium. The ideal semipermeable medium will not absorb any salt from the solution, but only water, but such perfection is probably seldom to be met with. If a semipermeable medium such as parchment paper be immersed in a solution, say, of sugar, less water is taken up or absorbed than is the case when the immersion is in pure water. The diminution in the amount absorbed is found to increase with the strength of the solution. It is at the same time found that the absorption or release of water by the semipermeable medium according as the solution is made weaker or stronger is accompanied by a swelling or shrinkage greater than can be accounted for by the water taken up or rejected. The amount of water absorbed by a semipermeable medium from a solution is found by experiment to depend upon the hydrostatic pressure. If the pressure be increased the amount of water absorbed by the semipermeable medium is increased. It is always thus possi-

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[1] Brit. Ass. Reports, **84,** 288 (1914).

ble by the application of pressure to force the semipermeable medium to take up from a given solution as much water as it takes up from pure water at atmospheric pressure. It is not possible for a mass of such a medium to be simultaneously in contact and in equilibrium both with pure water and with a solution all at one and the same pressure, seeing that the part of the medium in contact with the pure water would hold more water than that part in contact with the solution, and consequently diffusion would take place through the mass of the medium. If, however, the medium be arranged so as to separate the solution and the water, and provided the medium is capable of standing the necessary strain, it is possible to increase the pressure of the solution without increasing the pressure of the water on the other side. Thus the part of the medium which is in contact with the solution is at a higher pressure than that part in contact with the pure solvent; consequently the medium can be in equilibrium with both the solution and the solvent, for if the pressures are rightly adjusted the moisture throughout the medium is everywhere the same.

"The ordinary arrangement for showing osmotic pressure is a case such as we are considering, and equilibrium throughout the membrane is only obtained when the necessary difference in pressure exists between the two sides of the membrane. The conditions would eventually be reached no matter how thick the membrane was. It is sometimes helpful to think of the membrane as being very thick. It precludes any temptation to view molecules shooting across from one liquid to the other through some kind of peepholes in the membrane. The advantage of a thin membrane in practice is simply that the necessary moisture is rapidly applied to the active surface, thus enabling the pressure on the side of the solution to rise quickly, but it has no effect on the ultimate equilibrium. As far as that goes, the semipermeable membrane or saturated medium might be infinitely thick, or, in other words, there need be no receptacle or place for holding the pure solvent outside the membrane at all. In fact the function of the recep-

tacle containing the pure solvent is only to keep the medium moist, and is no more or less important than the vessel of water supplied to the gauze of the wet-bulb thermometer. It is merely to keep up the supply of water to the medium.

"The real field where the phenomenon of osmosis takes place is the surface of separation between the saturated semipermeable medium and the solution. Imagine a large mass of colloidal substance saturated with water and having a cavity containing a solution. The pressure will now tend to rise in the cavity until it reaches the osmotic pressure—that is, until there is established an equilibrium of surface transfer of molecules from the solution into the medium and back from the medium into the solution. No doubt the phenomenon as thus described occurs often in nature. It is just possible that the high pressure liquid cavities which mineralogists find in certain rock crystals have been formed in some such manner in the midst of a mass of semipermeable medium; the pure solvent in this case being carbon dioxide and the medium colloidal silica, which has since changed into quartz crystal.

"In considering equilibrium between a saturated semipermeable medium and a solution there seems to me to be a point which should be considered carefully before being neglected in any complete theory. That is, the adsorption layer over the surface of the semipermeable medium. We have seen that solutions are profoundly modified in the surface layers adjoining certain solids, through concentration or otherwise of the salts in the surface layer, so that the actual equilibrium of surface transfer of water molecules is not between the unmodified solution and the semipermeable medium, but between the altered solution in the absorption layer and the saturated medium. Actual determinations of the adsorption by colloids are much wanted, so as to be able to be quite sure of what this correction amounts to or even if it exists. It may turn out to be zero. If there is adsorption, however, it may be possible to account for part of the unexpectedly high value of the osmotic pressure observed at high concen-

trations of the solution, the equilibrium being, as we have seen, between the saturated medium and a solution of greater concentration than the bulk of the liquid, namely, that of the adsorption layer. In addition, when above the critical adsorption point, there may be a deposit in the solid state. This may produce a kind of polarized equilibrium of surface transfer in which the molecules which discharge from the saturated medium remain unaltered in amount, but those which move back from the adsorption layer are reduced owing to this deposit, thus necessitating an increase in pressure for equilibrium. If either or both of these effects really exist, it would seem to require that the pressure should be higher for equilibrium of the molecular surface transfer than if there were no adsorption layer and the unaltered solution were to touch the medium, but at the same time it should be remembered that there is a second surface where equilibrium must also exist—that is, the surface of separation of the adsorption layer and the solution itself. It is just possible that the two together cancel each other's action.

"Quantitative determinations of adsorption by solid media from solution are hard to carry out, but with a liquid medium are not so difficult. Ether constitutes an excellent semipermeable medium for use with sugar solution, because it takes up or dissolves only a small quantity of water and no sugar. A series of experiments using these for medium and solution has shown (1) that the absorption of water from a solution diminishes with the strength of the solution; and (2) that the absorption of water for any given strength of solution increases with the pressure. This increase with pressure is somewhat more rapid than if it were in proportion to the pressure. On the other hand, from pure water, ether absorbs in excess of normal almost in proportion to the pressure. Certainly this is so up to 100 atmospheres. This would go to confirm the suggestion made that the departure from proportionality in the osmotic pressure is attributable to adsorption. By applying pressure ether can be thus made to take up the same quantity of water from any given solu-

tion as it takes up from the pure water at atmospheric pressure. It is found by experiment that this pressure is the osmotic pressure proper to the solution in question."

It is quite clear that we can get osmotic phenomena in two distinct ways depending on whether we have a continuous film or a porous one. In the case of a continuous film it is essential that the solvent shall dissolve in the membrane and the solute shall not. Since the permeability is not dependent on adsorption, there is no reason why there should be any fundamental difference between the adsorption of a solute which does pass through the membrane and of one which does not pass through. If we have a porous film, we get osmotic phenomena only in case the pore walls adsorb the pure solvent and the diameter of the pores is so small that the adsorbed film of the pure solvent fills the pores full. Under these circumstances the dissolved substance cannot pass through the pores. On the other hand, if the dissolved substance can pass through the membrane, it must be adsorbed by the latter. There is therefore a fundamental difference between a solute which does pass through a porous membrane and one that does not in that the first is adsorbed by the membrane and the second is not. This way of looking at it makes Bartell's results perfectly intelligible; but it also shows that his conclusions must be modified to a certain extent. Since we are dealing with selective adsorption it cannot possibly be strictly true that osmotic pressure phenomena begin at the same pore diameter for all membranes and all solutions, though the fluctuations may well be small in many cases. Incidentally, it does not follow that all semipermeable membranes are porous because one is.

When castor oil is the semipermeable membrane, we are dealing unquestionably with a continuous film and adsorption plays no essential part in the question of permeability; but it is not so clear what we are dealing with when we have a rubber or a copper ferrocyanide membrane.

Kahlenberg[1] has shown that benzene, toluene, and

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[1] Jour. Phys. Chem., **10,** 141 (1906).

pyridine pass through a rubber membrane very readily while water does not. This is perfectly natural on the assumption that these liquids dissolve in rubber; but on the basis of pores it is difficult to understand why water should not pass through. One might hark back to the case of the oiled sieve and say that water does not wet rubber; but the difficulty is that water does wet rubber. The case of trichloracetic acid is also interesting. When dissolved in benzene it passes through a rubber membrane readily, whereas it passes through very slowly when dissolved in water. This is quite easy to explain if we are dealing with solution and very difficult if we are dealing with adsorption. Another interesting fact which may or may not have a bearing is that Küster[1] found that the distribution of ether between rubber and water could be represented by the equation $C_r/C_w^2 =$ const., whereas in all duly accepted cases of adsorption it is the concentration in the solid that carries the factor. While nothing is proved, I am inclined to think that a rubber membrane is not a porous one in the sense that Bartell's clogged cups are, and I believe therefore that when a rubber film acts as a semipermeable membrane, the solvent dissolves in the rubber and passes it essentially in that way. There are no published data which would enable us to tell anything about the copper ferrocyanide membrane; but my personal feeling is that it is more like the liquid diaphragm and the rubber diaphragm than like the clogged porcelain membrane. With the clogged porcelain membrane, the semipermeability depends undoubtedly on adsorption; but I believe it to be an interesting special case and not the general one.

In this discussion it has been assumed that the clogged membrane was strictly semipermeable. Diffusion from the solvent to the solution and the production of some osmotic pressure may take place even though the membrane is not semipermeable. It is merely necessary that the rate of flow from the solvent to the solution shall exceed the rate in the opposite direction. We may postulate that the adsorbed

[1] Zeit. phys. Chem., **13,** 445 (1890).

film in the pores is not pure water but is a very dilute solution. In that case water will pass in one direction and the solute in the other; but the more dilute the solution the more the osmotic flow will counterbalance the diffusion of the solution. If the adsorbed film is practically pure water, but the pore diameters are just large enough so that there is a thin core of uncharged solution, there will be a flow in both directions. In the later series of papers Bartell[1] is evidently working under conditions under which the dissolved substance passes through the membrane because he gets negative osmosis under certain circumstances. To what extent this negative osmose is a case of electrical endosmose cannot be discussed at this point.

Bigelow has urged that we have a capillary structure in the case of liquids and that a liquid may therefore be considered as a porous diaphragm. This does not seems to be a satisfactory point of view. Solution is certainly not a question of relative molecular sizes. The solubility of sugar in water and its insolubility in alcohol or benzene are certainly not due to the fact that liquid water is more porous than liquid alcohol or liquid benzene. If one is going to insist on a mechanical conception, we get solution when the dissolved substance is able to push aside and displace the molecules of the solvent. A fish does not swim through the holes in the ocean; he displaces the water. There is obviously no relation between the alleged porosity of a liquid and the formation of a colloidal solution and also none between the porosity of the liquid and the formation of a true solution.

The general results of this paper are as follows:

1. We may have osmotic phenomena with a porous diaphragm provided we have very marked negative adsorption and provided the diameter of the pores is so small that the adsorbed films fill practically the whole of the pores.

2. A porous diaphragm will act as a semipermeable membrane in case there is no measurable adsorption of the solute and in case the adsorbed films fill the pores completely.

[1] Jour. Am. Chem. Soc., **26**, 646 (1914); **38**, 1029, 1036 (1916).

3. In the usual case of a semipermeable diaphragm, we do not have a porous diaphragm and the semipermeability is due to the fact that the solvent dissolves in the diaphragm while the solute does not to any appreciable extent under the conditions of the experiment.

4. A liquid is not to be considered as a porous substance and solubility does not depend on porosity.

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ADSORPTION BY SOILS[1]

BY J. E. HARRIS

In a former paper,[2] the writer published the results of some experiments undertaken to throw some light on the cause of acidity in soils. The results of those experiments supported in every way the theory that acidity in soils is due to selective adsorption rather than to the presence of true acids. The experiments described in this paper have been undertaken to obtain more evidence concerning the phenomena of soil acidity and of adsorption by soils. Before taking up a discussion of the experimental work it will be well to describe briefly the properties of acid soils and to review the various theories concerning the cause of acidity.

Acid soils may be divided into two types. The first, which may be truly called an acid soil, will give an extract with water which is acid to litmus, indicating that there is present in the soil a soluble acid. This type of acid soil is comparatively rare.

The second type, which is the type considered in this paper, gives a water extract that is neutral to litmus, but gives a sharp acid action when a piece of sensitive litmus paper is brought into direct contact with the moistened soil particles themselves. These soils, although giving a neutral extract with water, will give a strongly acid solution when shaken with a neutral salt solution.

Concerning the cause of acidity in the first type of soil there can be no question. It is undoubtedly due to the presence of true acids, these acids manifesting themselves by giving an acid solution when the soil is extracted with water. Occasionally appreciable quantities of a mineral acid, such as sulphuric acid, are found in the soil extract, but usually the

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[1] The experiments described in this paper were carried out while the writer was temporarily employed at the Michigan Agricultural College Experiment Station. The paper is published by permission of the Director of the Station.

[2] Jour. Phys. Chem., 18, 355 (1914).

acid found is of organic nature. Formerly these organic compounds were given names such as humic, ulmic, crenic, and apocrenic acids. These compounds are described in the literature between 1825 and 1850.[1] Later work by Eggertz,[2] van Bemmelen[3] and others has shown that the so-called "acids" described by the earlier writers are not definite compounds at all, but complex mixtures of colloidal nature exceedingly variable in composition. However, Schreiner and Shorey,[4] Olin[5] and others have demonstrated beyond a question of doubt that definite compounds, some of them of an acid character, can be extracted from the soil. As noted above, however, the cases in which these compounds are present in sufficient quantities to give an acid extract are rare.

Acid soils of the second type are exceedingly common in occurrence as is indicated by the statement of Whitson and Weir[6] that two-thirds of the soils of Wisconsin are acid in character. Undoubtedly soil acidity is as common in Michigan and other middle western states as in Wisconsin. Formerly the acidity of these soils as well as those of the first type was explained by the presence of acids of the type of humic, ulmic, and crenic acids. This theory concerning the cause of acidity has gradually been abandoned for two reasons. The first is that, as noted above, it has been found that humic, ulmic, and crenic acids are not definite compounds at all. The second is that a very large part of the acid soils of the second type are upland sandy soils so deficient in organic matter that the acidity could not be ascribed to organic matter. In fact, Daikuhara[7] has found soils in Japan which, although devoid of organic matter, are acid in character. The writer[8] has

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[1] For the literature on this subject see Technical Bulletin 19, Michigan Experiment Station (1914).

[2] Biedermann's, Zent. Agr. Chem., **18,** 75 (1888).

[3] Land. Vers. Sta., **26,** 113 (1888).

[4] U. S. Bureau of Soils, Bulletins **47, 70, 74, 77, 80, 83, 87, 88** and **90.**

[5] Ber. deutsch. chem. Ges., **45,** 651 (1912).

[6] Univ. of Wis. Exp. Sta. Bull. No. **230.**

[7] Chem. Zeit., **32,** 1187 (1908).

[8] Loc. cit.

shown that soils from which all organic matter had been removed were more acid in character than in their original state. The acidity in such cases cannot be ascribed to the presence of organic acids whether they be of the nature of humic acids or definite compounds of the type extracted by Schreiner and his co-workers.

There are two hypotheses offered to explain the acidity of soils in such cases. According to one, the acidity is due to the presence of true acids, in some cases to organic acids and in others to silicates of an acid nature. According to this explanation, the fact that test-papers are not affected by water extracts of the soil is accounted for on the assumption that the acids are so insoluble that the litmus must be brought into direct contact with the soil particles to be affected. The fact that quite appreciable quantities of acid are liberated when solutions of soluble salts are shaken with the soil is explained on the assumption that the insoluble acids enter into double decomposition with the salt liberating the corresponding acid. That is to say, if the soil is shaken with a solution of potassium chloride for example, the insoluble acid would in part be changed over to the potassium salt and an equivalent quantity of hydrochloric acid would be set free.

There are certain fundamental objections to this theory. In the first place, if the acidity is due to the presence of a true acid, the water extract of the soil should give just as strong an acid action toward litmus as the moistened soil particles themselves. According to the generally accepted idea, an acid owes its properties to the presence of the hydrogen ion. Now it is known that if a piece of sensitive litmus paper be drawn carefully through the supernatant liquid so as not to touch the soil particles in the bottom of the receptacle, the paper will be unaffected. If, on the other hand, the paper be dragged over the surface of the soil particles or the mixture be agitated in such a way that the soil particles come into direct contact with the test-paper, the blue litmus is instantly reddened. If this effect is due to the presence of a true acid, in other words to the presence of the hydrogen ion, we must as-

sume that the hydrogen ions are held in some mysterious way to the soil particles themselves and are not free to migrate through the solution in the usual manner. If we cannot assume that the hydrogen ions are bound in this manner by the soil particles, then it is necessary to assume that the reddening of the litmus is due to something other than the hydrogen ions, in which case this something cannot be a true acid. Again, as mentioned above, these acid soils have the property of liberating free acids when shaken with solutions of neutral salts. If this is brought about by a double decomposition with the insoluble acids it means that an insoluble and slightly dissociated acid is reacting to liberate quite appreciable quantities of a soluble and highly dissociated acid, a phenomenon that is hardly conceivable in the light of the law of mass action.

These objections to the theory concerning the presence of true acids in those acid soils which give neutral water extracts have given rise to a second theory concerning the cause of the peculiar behavior of such soils. This theory is based on the assumption that the colloidal matter of the soil has the power of adsorbing selectively the cation from a neutral salt solution leaving an equivalent quantity of soluble acid in solution. If the soil is shaken with a solution of potassium chloride for example, it is assumed that the negatively charged colloidal matter of the soil will adsorb a certain amount of the positively charged potassium ions from the solution, setting free a corresponding amount of hydrochloric acid. This theory furnishes a plausible explanation for the action of soil toward litmus paper. The soil will adsorb the base of the blue litmus salt when the test-paper is brought into direct contact with the soil particles leaving the red acid dye on the paper. Since this theory does not assume the presence of a true acid, the water extract would be found to be neutral toward litmus, and this is found to be the case in a great majority of cases of soil acidity. More will be said concerning the mechanism of selective adsorption later.

In the paper mentioned above, the writer described some

experiments which were undertaken to secure some positive
evidence in favor of the adsorption theory. It was shown
that, when samples of a soil were shaken with solutions of
different salts such as sodium nitrate, and potassium chloride,
different quantities of acid were set free, indicating that differ-
ent quantities of the cation were taken up by the soil in the
two cases. It might be argued that the difference in quantity
of acid set free is a function of the strength of the two acids
involved. However, if this were the case, we would find
that with successive applications of the salt solution to the soil,
the total quantity of acid set free in the successive applica-
tions of the two salts would approach the same limit if the
change were brought about by a double decomposition with
any free acid that is present in the soil; this limit would be
measured by the quantity of free acid in the soil. However,
it was found that the total amount of acid obtained in the suc-
cessive applications of potassium chloride in the one case and
of sodium nitrate in the other did not approach the same
limit. Instead, with each additional application, the ratio
of the total quantity of acid set free in the case of potassium
chloride to that in the case of sodium nitrate became greater.
This indicated that some change other than double decompo-
sition with a fixed quantity of some insoluble acid was re-
sponsible for the liberation of the acid.

Again when a soil was treated with barium chloride solu-
tion, it was shown that the barium taken up by the soil could
be removed almost quantitatively by a single application of
$N/20$ hydrochloric acid, although it could not be washed out
by persistent washing. If the action between the barium
chloride and the soil is one of double decomposition, we must
conclude that the acid present in the soil forms a salt with the
barium that is more insoluble than the acid which is itself
so insoluble that it cannot be washed out in measurable quan-
tities even with several days of continuous washing. It
would be hard to conceive of anything more insoluble than this
barium salt. We would not then expect this action to be re-
versible to any appreciable extent. It was found, however,

as stated above, that the barium could be changed back to the soluble chloride by treating the soil with dilute hydrochloric acid. This fact would indicate that the barium is held by the soil in some other form than an insoluble barium salt.

E. Truog[1] has criticized the conclusions drawn from the above experiments. Concerning the first experiment, Truog asserts that the fact that different quantities of sodium and potassium were taken up by the soil can be accounted for by various "side reactions." He suggests as some of these side reactions, different rates of hydrolysis of the salts formed by different bases, action of organic matter, "latent acidity," etc. Wherever his own results or those of other experimenters do not agree with his theory, he dismisses the non-agreement on the ground of side reactions. He does not show that these side reactions actually take place. In another experiment, he attempts to avoid these side reactions by using small quantities of soil with large volumes of salt solutions. He finds that using sodium chloride, potassium chloride, barium chloride, and calcium chloride, the quantities of acid liberated measured in terms of cc of $N/25$ NaOH, were, respectively, 1.2, 1.4, 1.4, and 2.0 in the case of a silt loam soil, and 1.9, 1.9, 1.9, and 2.7 in the case of a peat soil. He concludes from this that "the reactions due to soil acidity take place according to chemical equivalence and exhibit all the properties of true chemical reactions." However, an examination of his figures shows that 67 percent more acid is liberated in the calcium chloride solution than in the sodium chloride in the case of the loam and 43 percent more in the case of the peat soil.

This, however, has very little to do with the question at issue. Even though a particular soil does take up nearly equivalent quantities of different bases, this fact does not show that all soils will behave in the same manner nor does it show that the action is not one of adsorption. Certainly in the soils investigated by the writer much greater quantities

[1] Jour. Phys. Chem., **20**, 457 (1916).

of acid were liberated from potassium salts than from sodium
salts. Of course, these results can be dismissed with the magic
phrase "side reactions," but until these side reactions are
actually shown to take place and that these can be avoided
in the way Truog suggests, about the only conclusion that
can be drawn is that different types of soil vary in their power
of liberating acids from various salts.

With regard to the experiment in which the writer has
shown that the adsorbed barium may be recovered by the ad-
dition of a dilute acid, Truog says "Harris, apparently, for-
gets that in the first reaction an overwhelming mass of barium
chloride was used and the reaction forced as a consequence
to the right. In the second reaction the excess of barium
chloride had previously been removed and now a large excess
of hydrochloric acid is added and, to be sure, the reaction is
reversed and forced to the right. The results are entirely in
accord with the law of mass action and serve as evidence in
favor of the existence of true acids as the cause of soil acidity."

In order to determine the validity of Truog's conclusion,
it will be well to consider once more the nature of the substances
involved. If there is an acid present in the soil, its insolubility
is indicated by the fact that when the writer subjected a
sample of acid soil to continuous washing for a period of two
weeks, its power for liberating an acid from a neutral salt was
just as great as before the washing, thus showing that none
of the "acid" had been removed by the long-continued wash-
ing. The fact that barium chloride reacts with this very weak
and insoluble acid liberating a very large quantity of a strong
acid, makes it necessary that the barium salt be even more
insoluble than the acid itself. This would make the barium
salt about as insoluble a product as any that can be imagined.
This being the case, we would not expect to render appreciable
quantities of the barium soluble by treatment with hydro-
chloric acid, if the barium compound were formed by double
decomposition, whereas the writer found that with $N/20$
hydrochloric acid the barium could be recovered almost
quantitatively. The fallacy of Truog's conclusion concerning

the experiment may be seen by considering a similar instance with substances with which we are somewhat more familiar. Starting with barium oxalate and adding sulphuric acid, we would get of course barium sulphate and oxalic acid, the barium oxalate disappearing. Now according to Truog's reasoning, if we remove the sulphuric acid completely and add a slight excess of oxalic acid, the barium sulphate should be changed back almost completely to barium oxalate. Of course this could not happen. It is impossible to believe that any acid of the character that might be present in an almost absolutely insoluble condition in the soil can react with a soluble salt and liberate large quantities of a strong acid. And even if this were possible (as it might be if the barium salt were many times as insoluble as the corresponding acid) it would certainly be impossible to carry the barium back into solution by removing the soluble salt and somewhat increasing the concentration of hydrochloric acid above that liberated by the action of the soil on the barium chloride.

Truog goes farther, and states that the "selective adsorption from the common, simple, stable, neutral salts has never been demonstrated conclusively." Also that "various properties having no existence in either pure chemistry or physics are ascribed to colloids in order that certain phenomena may be explained without going to the trouble of finding the real cause." Since the only property of colloids under discussion is their power for selectively adsorbing ions from solutions of electrolytes, he would thus place in this category such chemists as Whitney and Ober, Cameron, Billitzer, Freundlich, Michaelis and many others who have worked on colloidal precipitation.

In the paper above mentioned, the writer likened the action of the soil toward solutions of salts to that of colloidal arsenic trisulphide. Picton and Linder[1] first observed that in the coagulation of arsenic trisulphide by barium chloride solution, the precipitate carries down with it a certain amount of barium, an equivalent amount of hydrochloric acid being liberated in the solution. Truog calls attention to the fact

[1] Jour. Chem. Soc., **67**, 63 (1895).

that Picton and Linder[1] explain this action on the basis of a double decomposition. While it is true that Picton and Linder do offer such an explanation it is also true that their explanation has not been generally accepted. In fact, Whitney and Ober[2], Freundlich,[3] Taylor[4] and practically all who have written on this subject regard the action of electrolytes with arsenic trisulphide as a case of adsorption.

But granting that the interpretation in this particular experiment is doubtful, another example may be cited concerning which there can be no doubt. Freundlich and Losev[5] have shown that when charcoal is treated with methyl violet (an organic chloride) the dye is adsorbed in the form of the organic base, and an equivalent quantity of hydrochloric acid is set free in the solution. The base thus adsorbed is not soluble in water, but may be easily removed by acids, alcohol, pyridine and other organic solvents. Now methyl violet is a strongly dissociated electrolyte and is not hydrolyzed in water solution, and in this regard is comparable to barium chloride. The action is in every way analogous to the action of arsenic trisulphide, soils and other colloids toward electrolytes. There is the difference that the methyl violet has an organic cation instead of a metal cation, but it is not possible to endow it with special properties for this reason. Freundlich[6] has found that arsenic trisulphide has the same effect on dyes as has the charcoal, and finds that the adsorption of metallic ions follows the same law as does the adsorption of the base from such dyes as methyl blue.

The question next arises as to why any substance should selectively adsorb any ion. In seeking an explanation for the selective adsorption of ions, we must keep in mind certain well-known properties of colloids. With very few exceptions colloidal substances (either in solution or in suspension)

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[1] Jour. Chem. Soc., **87**, 1914 (1905).

[2] Jour. Am. Chem. Soc., **67**, 63 (1901).

[3] Kapillarchemie.

[4] Chemistry of Colloids, p. 104, Longmans, Green and Co.

[5] Zeit. phys. Chem., **59**, 284 (1907).

[6] Loc. cit.

carry electric charges, in a few cases positive but in most cases negative. Soils, kaolin, and practically all suspensions are negatively charged. The presence of this charge is shown by the migration of the particles in suspension under an applied electromotive force. Again this colloidal condition seems to depend upon this charge because as soon as the charge is neutralized by any method, and the colloid becomes electrically neutral (the isoelectric point), it is coagulated. This precipitation by neutralization of the charge carried may be brought about (1) by the addition of electrolytes, in which case it is always the ion carrying an opposite charge to that of the colloid that causes the precipitation, (2) by the addition of a colloid of opposite charge in which case both colloids are precipitated, (3) by the action of negatively charged β-rays in the case of positively charged colloids. In this latter connection,[1] it has been shown that the negatively charged rays will precipitate certain positively charged colloids, and will increase the mobility of certain negatively charged substances.

The facts concerning the precipitation of colloids by electrolytes, such as the influence of valence, etc., are too well known to need further discussion here, but the question as to whether that portion of the precipitating ion that is almost invariably carried down with the colloidal precipitate, is held enmeshed by the colloid through adsorption or through a chemical process is the important question in connection with the present problem. There are two facts that tend to support the adsorption hypothesis. First, the fact that the precipitation of one colloid by another of opposite charge is accompanied also by the precipitation of the latter, would lead us to believe that the precipitation of a colloid by an oppositely charged ion should be accompanied by the enmeshing of a sufficient quantity of that ion to neutralize the charge on the colloid. Second, in the case mentioned above, of the action of charcoal, silk, wool, and cotton on dyes such as methyl violet we have undoubted cases of adsorption of the cation,

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[1] Hardy: Jour. Physiology, **29**, 29 (1903).

this adsorption being accompanied by the liberation of an equivalent quantity of acid.

Freundlich[1] has suggested an explanation of these facts based on Perrin's[2] work. This explanation accounts for the charge carried by the colloid, the adsorption of the cation, and the liberation of an equivalent quantity of an acid. Perrin has shown that the presence of the hydrogen or hydroxyl ions has an important influence on the charges carried by solid particles in contact with water. In contact with acids and high concentrations of the hydrogen ion, the solid particles become positively charged, while in contact with bases and high concentrations of the hydroxyl ions the particles become negatively charged. Freundlich explains this on the supposition that when a body in suspension is positively charged it has adsorbed hydrogen ions, these hydrogen ions forming one layer in a system of Helmholtz double layers, the other layer being formed by the acid ions, these two layers, of course, being an infinitesimal distance apart. In case the substance carries a negative charge, it is the hydroxyl ions that will form the layer on the surface of the substance thus giving it its charge. In case the substance is charged in contact with water and in the absence of bases and acids, it is the hydrogen and hydroxyl ions of the water that are responsible for the charges. In the case of a negatively charged body the hydroxyl ions form the layer next to the solid and the hydrogen ions the other. In the case of the positively charged body, the conditions are reversed. To explain this preferential adsorption, it is only necessary to recall that any substance which will lower the surface tension of a liquid in a system consisting of a solid and a liquid will be mechanically adsorbed.[3] If the hydrogen ion lowers the surface tension of the liquid in contact with the solid it will be adsorbed and, of course, impart to the adsorbing surface its charge. If the hydroxyl ion lowers the surface tension it will be adsorbed and the charge

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[1] Zeit. phys. Chem., **59**, 284 (1907).

[2] Comptes rendus, **136**, 1288, 1440; **137**, 513, 564 (1903).

[3] See Michaelis: Dynamics of Surfaces, p. 22, E. and F. N. Spon.

will be negative. Since most suspensions are negatively charged, the hydroxyl ion must, in most cases, form that part of the double layer next to the particles. If the charge on the suspended particles is in any way neutralized, the suspension is flocculated. If the suspended particles are brought into contact with an electrolyte, that ion again which has the greatest effect in lowering the surface tension will tend to pass into the inner layer. In most cases apparently, when the electrolyte is a salt, it is the metal ion that is adsorbed. Of course, upon passing to the inner layer it will counterbalance the charge *within this layer* and the suspension will become electrically neutral, permitting the particles to coalesce and settle out, the precipitate carrying down with it the cation and the hydroxyl ion. The balancing of the charge due to the hydroxyl ions in the inner layer will set free the hydrogen ions of the outer layer. These will pass into the solution forming with the acid ions of the electrolyte a free acid.

This hypothesis of Freundlich's furnishes a better explanation for the facts concerning selective adsorption than any of the others that have been advanced. To suppose that the colloid in being coagulated simply carries down with it the ion of charge opposite to its own, would leave free ions with unbalanced charges in solution. To suppose as does Parker[1] that the colloid hydrolyzes the salt, and carries down the base leaving the acid in solution, would not account for the neutralization of the charge on the colloid. Also it would give to the colloid a power of decomposing salts, for which we would have no adequate explanation. Freundlich's hypothesis has the advantage that it furnishes an explanation for the charge on the colloid, for its precipitation by an electrolyte, and for the carrying down by the precipitate of the ion carrying the opposite charge.

Another hypothesis to explain the action of soils toward salt solutions has recently been advanced by Frank E. Rice,[2] who suggests that the acid set free when a soil is shaken with

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[1] Jour. Ag. Research, **1**, 179 (1913).
[2] Jour. Phys. Chem., **20**, 214 (1916).

a neutral salt is a result of the hydrolysis of aluminium salts formed by the displacement of aluminium ions by the cation of the salt. This phenomenon undoubtedly does account for a large part of the acid set free in the salt solution, for it has been noticed by all who have experimented with soils of this type that large quantities of aluminium salts are present in the solution after a soil has been shaken with a neutral salt solution. However, this hypothesis cannot explain all the properties of such soils. For example, the writer[1] has shown that if a soil be treated with a dilute acid, and this dilute acid washed out, the soil has a very much greater power for liberating acids from neutral salt solutions than before. The effect of the acid would be to remove any adsorbed bases, including aluminium so that if Rice's hypothesis were correct, their power for liberating acid in a salt solution should be decreased by such treatment rather than increased. This hypothesis also fails to account for the power of peat soils of liberating an acid from a salt solution.

Sharp and Hoagland[2] have recently used the hydrogen electrode for the determination of hydrogen ion concentrations in soil solutions. They found that soil solutions from acid soils showed higher hydrogen ion concentrations than did those from neutral soils. They also found that the hydrogen ion concentration was materially increased by the addition of neutral salts in the case of acid soils. They conclude that acidity in soils is due to the presence of true acids. The writer wishes to call attention to the fact that in acid soils (meaning by this, soils deficient in basic material), the conditions are especially good for the accumulation of small quantities of acid due to the deficiency of basic material for them to combine with. Under ordinary conditions of drainage there might be sufficient quantities of acid accumulated to be detected by the hydrogen electrode but not by litmus. It cannot be concluded, however, that this small quantity of acid can be the cause of the liberation of large quantities of acid when treated

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[1] Loc. cit.

[2] Jour. Ag. Research, **7**, 123 (1916).

with a salt, nor can those experiments explain the fact that, although litmus is not affected by the soil solution, it is sharply acted upon by the soil particles themselves.

The experiments described in this paper were undertaken with a two-fold purpose; first, to secure additional evidence as to whether the cause of acidity (where such acidity is characterized by a neutral soil solution, but acid action when test-papers are brought into direct contact with the soil particles) is due to colloidal adsorption or to the presence of true acids; second, to secure data that might throw some light on the action of fertilizer salts.

It is known that in cases of adsorption by colloids, whether from solutions of dyes or from solutions of electrolytes, the quantitative relations are expressed by the equation $x/m = ac^{1/n}$ where x is the mass of the material adsorbed, m the mass of the adsorbing substance, c the concentration of the solution with respect to the material adsorbed, and a and n are constants characteristic of the substances used. This formula may be written in the form $c_1/c_2^{1/n} = k$, in which form it is an empirical modification of Nernst's partition law, which is formulated thus, $C_1/C_2 = K$. This latter equation gives the equilibrium conditions when a substance is shaken up with two immiscible liquids in each of which it is soluble. There is a second adsorption formula that has been developed by Freundlich[1] partly on theoretical and partly on empirical considerations. This formula is expressed thus: $\frac{v}{m} \log \frac{a}{a-x} = \alpha \left(\frac{v}{a}\right)^{-1/n}$, where v represents the volume of solution, m the mass of adsorbing material, a the total quantity of adsorbable material, x the quantity adsorbed, and α and n are constants. However, by the expansion of the terms involved, Freundlich showed that the first adsorption equation expressed above could be derived from his. The first equation is the one most often used in work on adsorption. The value[2]

[1] Zeit. phys. Chem., **57**, 385 (1906).

[2] Freundlich: Kapillarchemie, p. 150.

of $1/n$ usually lies between 0.1 and 0.5. This formula gives us a good method for testing the action in the case of the soil to determine whether we have a case of adsorption or one of chemical reaction.

The test was applied to a soil of the sandy loam type. In preparing the soil samples, the soil was air-dried and put through a 20-mesh sieve, every precaution being taken to secure as nearly uniform samples of the soil as possible. 50-gram samples of the soil were treated with solutions of barium chloride varying in concentration from 0.8 N to 0.01 N, the mixtures being shaken at intervals for a period of twenty-four hours. The volume of solution used in each case was 125 cc. The solution was analyzed before and after application to the soil, the quantity of barium adsorbed being determined by difference. In calculating the results, the equation used was $x = ac^{1/n}$. The use of this simpler form of the equation given above is made possible by the fact that the mass, m, of the adsorbing substance was kept constant. The elimination of this quantity merely changed the value of the constant a. The values of $1/n$ were calculated and the results are shown in the following table. The concentrations of the barium ion were calculated from the values given in conductivity tables for barium chloride solutions.

TABLE I

Normality of BaCl$_2$ sol.	Conc. of Ba ions. Grams per 100 cc	Total quantity of Ba adsorbed	$1/n$
0.8	3.3175	0.2375	0.437
0.4	1.8133	0.1983	0.374
0.2	0.9849	0.1550	0.395
0.1	0.5233	0.1125	0.414
0.07	0.3778	0.1109	0.372
0.04	0.2253	0.0819	0.405
0.02	0.1175	0.0580	0.421
0.01	0.0611	0.0413	0.437

A similar experiment was performed with kaolin which had been treated with $N/20$ hydrochloric acid, the excess acid being

then removed by careful washing. This treatment is the same as that applied to the kaolin used in the experiments described in a previous paper.[1] The kaolin before treatment with the acid was perfectly neutral in its behavior, but after the treatment with the acid, although washed until the wash water was found to be neutral, had the same power as the acid soils of liberating a soluble acid when shaken with a solution of a neutral salt. The results are given in Table II.

TABLE II

Normality of $BaCl_2$ sol.	Conc. of Ba ions. Gms. per 100 cc	Quantity of Ba ions adsorbed	$1/n$
0.1	0.5233	0.1065	0.275
0.07	0.3778	0.0982	0.274
0.04	0.2253	0.0885	0.262
0.02	0.1175	0.0714	0.274
0.01	0.0611	0.0567	0.284

The above results show values for $1/n$ that agree remarkably well especially when it is remembered that it is extremely difficult to get exactly uniform samples, particularly in the case of the soil. The fact that the values of $1/n$ are so nearly constant, indicates that the action is one of adsorption in both cases.

It was next undertaken to determine the power of adsorption on the part of the soil for various cations. As a preliminary to this experiment, samples of various soils were treated with barium chloride solution to determine whether or not the acid radical is adsorbed. In no case was there any evidence of adsorption of the chloride ion, indicating that the soil adsorbs only the positive ion. The salts used in this experiment were sodium chloride, potassium chloride, calcium chloride, barium chloride, manganese chloride, magnesium chloride, and aluminium chloride. To determine the quantities of the cations adsorbed, 50-gram samples of soil were treated with 125 cc of $N/10$ solutions of each of the above

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[1] Loc. cit.

salts. The solutions were left in contact with the soil for a period of twenty-four hours, being frequently shaken during that period. The solutions were analyzed before and after treatment of the soil, and the quantities adsorbed determined by difference.

TABLE III

Solution	Quantity of cation adsorbed	No. of equivalents adsorbed
KCl	0.0395	0.00101
NaCl	0.0041	0.00013
CaCl$_2$	0.0134	0.00067
MnCl$_2$	0.0177	0.00064
MgCl$_2$	0.0057	0.00047
AlCl$_3$	0.0113	0.00125

From the above tables, it may be seen that the calcium, manganese and magnesium are adsorbed in almost equivalent quantities, while the potassium and aluminium are adsorbed in larger quantities and the sodium in much smaller quantities. It is of interest to note that the quantities of the ions adsorbed follow closely the valence rule for the precipitation of colloids, the potassium being excepted. The writer can offer no explanation for the anomalous behavior of the potassium. Whether there is any connection between the high adsorptive power of the soil for this element and the important role played by this element in influencing the fertility of the soil is hard to say. Presumably the potassium would have a greater effect on the physical properties of the soil than would the sodium or the divalent ions Ca, Mn or Mg. On the other hand the Al would be more effective so far as its flocculating power is concerned but the beneficial effect of this would be destroyed through the hydrolysis of aluminium salts and the consequent setting free of soluble acids.

To determine the extent to which the various ions m replace adsorbed potassium ions, a large quantity of soil w treated with normal potassium chloride solution, the two being shaken together for several hours. The solution was then re-

moved by centrifuging. This was repeated six times to insure the adsorption of as large a quantity of potassium as possible. The soil was thoroughly washed to remove the greater part of the soluble potassium. After drying, nine 50-gram samples were treated as follows:

No.	Treated with
1	200 cc distilled water
2	200 cc $N/10$ NaCl
3	200 cc $N/10$ NH$_4$Cl
4	200 cc $N/10$ CaCl$_2$
5	200 cc $N/10$ MnCl$_2$
6	200 cc $N/10$ MgCl$_2$
7	200 cc $N/10$ AlCl$_3$
8	200 cc water with 1.72 g CaSO$_4$.2H$_2$O
9	200 cc water and 1 g CaCO$_3$

The samples of soil were left in contact with the solutions, with occasional shaking, for a period of seventy-two hours, after which the solutions were drawn off and the quantity of potassium determined. The results are shown in the following table:

TABLE IV

Sample No.	Treated with	K$_2$O found in solution	K$_2$O liberated by action of solution
1	H$_2$O	0.0092	—
2	NaCl	0.0393	0.0301
3	NH$_4$Cl	0.0568	0.0476
4	CaCl$_2$	0.0511	0.0419
5	MnCl$_2$	0.0514	0.0422
6	MgCl$_2$	0.0413	0.0321
7	AlCl$_3$	0.0617	0.0525
8	CaSO$_4$	0.0510	0.0418
9	CaCO$_3$	0.0322	0.0230

From the above table it may be seen that large quantities of the potash held adsorbed by the soil are liberated upon treatment with various salt solutions, and that the quantity varies with the salt solution used. Aluminium chloride is

found to liberate the greatest quantity followed in order by ammonium chloride, manganese chloride, calcium chloride, calcium sulphate, magnesium chloride, sodium chloride and the suspension of calcium carbonate in water. The order for the ions Al, Mn, Ca and Na is the same as that found in Table III. This was to be expected because the ability to liberate potassium held adsorbed by the soil should depend directly upon the relative tendencies of the different ions for being adsorbed.

It is possible that there is some connection between this displacement of potassium, held adsorbed by the soil, by other ions, and the beneficial effect noted by a number of experimenters upon the addition of gypsum, sodium chloride, and manganese salts to the soil. If such additions are beneficial because of the power of these substances to displace adsorbed potassium, the beneficial effect should be a temporary one, and such has usually been found to be the case.

To determine the effect of the presence of one ion upon the adsorption of another, three samples of soil were treated as follows: No. 1 with 200 cc of $N/10$ KNO_3, No. 2 with 200 cc of $N/10$ $CaCl_2$ and No. 3 with 100 cc of $N/5$ KNO_3 and 100 cc of $N/5$ $CaCl_2$. In No. 3 after mixing the solutions of KNO_3 and $CaCl_2$, the soil was, of course, in contact with a solution that was tenth normal with regard to both salts. The quantities of the ions adsorbed are shown in the following table:

TABLE V

	Quantity of K_2O adsorbed	Quantity of CaO adsorbed	No. of equivalents adsorbed	
			K_2O	CaO
No. 1	0.0471	—	0.0010	—
No. 2	—	0.0245	—	0.00087
No. 3	0.0347	0.0190	0.00074	0.00067

It is seen from these results that the quantity of one ion adsorbed is materially decreased by the presence of another ion, but the amount of decrease does not correspond to the

amount of the second ion adsorbed. In other words the sum of the equivalents adsorbed from the mixture is greater than the number of equivalents adsorbed from either solution alone. This would indicate that a soil that had adsorbed all that it could of one ion, would still retain some power of adsorption for another ion, over and above that adsorbed by the displacement of the first ion.

Summary

It has been shown that, when a soil or kaolin is treated with salt solutions of varying concentrations, the quantities of the cation adsorbed follow very closely the adsorption isotherm represented by the equation $x/m = ac^{1/n}$, indicating that the action is one of adsorption and not of double decomposition.

When the soil was treated with different salt solutions it was found that the number of equivalents of the different cations adsorbed was not the same. The cations with reference to their tendency for being adsorbed occurred in the order: Al, K, Ca, Mn, Mg and Na. The numbers for the ions Ca, Mn and Mg were very nearly the same. It is observed that the metals with the exception of the potassium occur in the order of their valence and that metals of the same valence give practically the same values.

It was found that a soil that had adsorbed large quantities of potassium, would give part of this up when treated with various salt solutions. In the case of the solutions tried it was found that, with reference to their ability to set free adsorbed potassium, the salts occurred in the following order: $AlCl_3$, NH_4Cl, $MnCl_2$, $CaCl_2$, $CaSO_4$, $MgCl_2$, $NaCl$, $CaCO_3$.

When the soil was treated with a mixture of salts it was found that the amount of each ion adsorbed was cut down by the presence of the other. The total number of equivalents adsorbed from the mixture was greater, however, than from either of the salts alone.

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CAPILLARY PHENOMENA AND SUPERCOOLING

BY S. LAWRENCE BIGELOW AND EDWARD A. RYKENBOER.[1]

PART I—SUPERCOOLING IN CAPILLARY TUBES

Introduction

In mountainous regions the existence, at a definite altitude; of a clearly marked "tree line," indicates that above this the average temperature is too low for the trees to withstand. Certain forms of vegetation cannot survive the winter above certain latitudes. It would appear to be a logical conclusion that the completeness with which all moisture within the tree or plant is frozen is at least one factor determining whether it lives or dies.

Under certain conditions liquids may be supercooled many degrees below their freezing points without solidification. It occurred to us that sufficient smallness of cells or capillary tubes might make possible a degree of supercooling such that at least some of the contained moisture did not freeze and that this might be the reason that some plants or trees were not "winter killed," but resumed their growth in the spring. In winter, trees and plants are frequently subjected to temperatures below the freezing point of the dilute solutions in their cells and pores. Trees give off moisture in winter at low temperatures and the amounts given off are more than can be explained by the vaporization of the ice present in the tree as a result of freezing, which indicates that there must be some circulation of liquids, though this may be small in amount. That the contents of the larger vessels freeze solid is doubtless true but whether the contents of the very minute ones freeze also is not so certain. If they do not, they could furnish the small amount of circulation which appears to be maintained. When different specimens of a single variety or tree growing at different altitudes are compared, it is found

that the capillary tubes become progressively smaller as the height at which the tree grows is increased. This seems to point to a natural fortification against the lower temperatures experienced at high altitudes. At any one altitude the pores in the summer wood are smaller than those formed in spring, but since the year's growth is very small this would not necessarily indicate that the smaller tubes were formed later in the season as a preparation for winter. We were unable to find any exact data bearing on these points, indeed we did not find any reference to the considerations just outlined, in our examination of the literature, either botanical, physicochemical or physical.

Furthermore, the question of pore size as determining, if it does determine, the degrees of supercooling possible without solidification, may be significant in connection with cold storage. For it is well known that many food products, after being frozen and then thawed, are less palatable. Possibly for each substance there is a temperature, below which it should not be brought.

The subject seemed to us of interest amply sufficient to justify a careful study of the amount of supercooling obtainable in capillary tubes and we hoped we might possibly succeed in formulating the degree of supercooling as a function of the diameter of the tube.

Discussion of Supercooling

The literature upon the subject of supercooling in capillary tubes is very meagre and is confined practically to a single contribution by H. C. Sorby.[1] He made a brief study of the temperatures at which water froze in capillary tubes of different diameters. He did this because he observed that in quartz cavities, liquids, that he supposed to be water, remained in the fluid state far below the freezing point of water. In tubes from $1/4$ to $1/40$ of an inch in diameter the freezing point was found to be about —6° C, in tubes smaller than $1/40$ of an inch he found he could carry the super-

[1] Phil. Mag., [4] **18**, 105 (1859).

cooling much further and in tubes of a diameter varying from 1/200 to 1/300 of an inch water froze at —17° C. On the other hand he found that there was no decided difference in the point at which freezing occurred in tubes varying from 1/200 to 1/700 of an inch nor in tubes with diameters from 1/4 to 1/40 of an inch. However, while the values for the tubes included in each of these ranges were the same, the two sets of readings were different. No conclusions were arrived at nor was any explanation offered for the phenomenon.

Van der Mensbrugghe[1] refers to supercooling in capillary tubes, among a number of other facts, which he uses as examples to demonstrate the application of a formula derived from thermodynamical considerations. The formula follows:

$$K = \frac{k - AtS \frac{d^2T}{dt^2}}{VX}$$

K   = specific heat.
k   = specific heat if surface has no potential energy.
A   = thermal equivalent of the unit of work.
t   = absolute temperature.
S   = free surface.
T   = potential energy of surface of contact (of a solid and a
       liquid which wets it).
V   = volume.
X   = specific gravity of the liquid.

The exact form of the function which expresses T by means of t for any liquid whatever is not known, but for a given liquid, the values of the coefficients of an equation such as $T = \alpha + \beta t + \gamma t^2 + \ldots$ can be obtained. According to Van der Mensbrugghe the values of β and γ for water are very small, and permit the powers of t higher than the second to be neglected. For the same liquid $\frac{d^2T}{dt^2}$ is negative and from this it follows that the quantity of heat to be supplied or taken away from unit weight of water, to raise or lower the temperature one degree, in general increases with t and also with S. Consequently it will be necessary to supply or withdraw much more heat to raise or lower the temperature one

[1] Phil. Mag., [5] **2**, 450 (1876); **4**, 40 (1877).

degree, if the total surface of a given mass is increased by any means, such as dividing it into many small spheres or introducing it into a capillary tube.[1]

In capillary tubes it is necessary to ascertain the sign $\frac{d^2T}{dt^2}$, in order to foresee the quantity of heat necessary for a variation of potential energy in the surface of contact between the liquid and walls. If the sign is negative, we must conclude that K increases with the surface S and consequently the smaller the tube diameter the larger will be the value of K. However, $\frac{d^2T}{dt^2}$ is a continuous function and for any decided difference in S/V there ought to be a corresponding difference in K, which would mean a difference in the supercooling, the other conditions remaining unchanged. A consideration of Sorby's results shows that this is not the case, since the diameters vary widely over ranges of equal supercooling values: the value S/V changing greatly with no corresponding change in supercooling. It seemed possible that Sorby's results were not accurate or that he had omitted to consider some important condition or source of error. But our experiments, described later, tend to confirm his results in this particular, and it becomes evident that the formula, as given, is of doubtful value, at least in its application to liquids in capillary tubes.

Although supercooling in capillary tubes has received so little attention, the general subject of supercooling and the conditions under which a supercooled liquid will crystallize

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[1] The ratio S/V increases as the volume of the mass diminishes, and, consequently, since d^2T/dt^2 is negative, the smaller the diameter of the mass or drop the greater will be the value of K. Van der Mensbrugghe believes that this explains how M. Mousson (Bibl. Univ. de Genève, **3**, 296 (1758)) was able at very low temperatures to keep drops of water of less than $1/2$ mm diameter in the liquid state, when disposed upon a surface which they did not wet. In the same way, Tomlinson (Students' Manual of Natural Philosophy, p. 553) could see minute drops of water, alcohol and ether roll upon the surface of a fixed oil raised to more than 200° C.

In this connection it can be shown that the sign d^2T/dt^2 changes under certain conditions: for water the change occurs in the vicinity of the maximum density.

spontaneously has been the subject of a good deal of study. Summarizing the results we may say that the spontaneous crystallization of a supercooled. liquid depends upon two factors:

(a) On the spontaneous power of crystallization: this is determined, and can be measured, by the number of centers of crystallization which are formed per unit of time in unit mass of the liquid.

(b) On the velocity with which the boundary between liquid and crystal is shifted (i. e., velocity of crystallization).

Crystallization[1] in a supercooled liquid never occurs homogeneously throughout the whole mass of the liquid but always begins at certain points or centers of crystallization, the number of which depends upon the amount and duration of the supercooling and the volume of the supercooled mass. Crystal threads grow outwards from these centers and spherical crystal aggregates result.   In many substances the number of centers can be determined by counting the spherical crystals, each crystal aggregate containing a center of crystallization. For this purpose the material, enclosed in a thin-walled glass tube, is heated just above the melting point and is then rapidly cooled 40° to 80°.   Then the centers usually begin to appear. If they appear too slowly the tube can be warmed slightly and the number of centers will be increased, but the velocity of crystallization increases also, so that the whole mass tends to crystallize when the first center appears and the counting is soon ended.   With increasing initial supercooling the number of centers formed per time and temperature unit increase at first to a maximum, but at temperatures about 100° below the melting point the number formed per unit time decreases rapidly.   This behavior is well shown in the case of piperin as is manifest in the two tables following:[2] The amount of substance used in each case was 1/8 cc. The melting point of piperin is 129° C.

[1] Tamman: Zeit. phys. Chem., 25, 443 (1898).
[2] Tammann: Loc. cit.

TABLE I

Cooled quickly to $t°$ C	Time Minutes	No. of centers
35.1	2	0
	4	2
	8	3
	12	5
40.2	2	4
	4	10
	8	19
	12	23
45.1	2	1
	4	3
	8	5
	12	7

TABLE II

$t°$	No. of centers	
25.2	38	32
30.1	73	62
35.2	102	96
40.1	132	141
45.2	106	111
50.2	92	96
55.3	85	88
60.1	52	43
65.2	27	24
70.2	8	7
75.1	0	1

In Table II the number of centers given is in every case the number which appeared in exactly two minutes.

Table III shows the relation between the volume of the liquid and the number of crystal nuclei.

TABLE III

t	Cylinder I 0.25 cc	Cylinder II 0.5 cc	Cylinder III 1.2 cc
0	1	1	18
20	4	5	58
40	39	50	148
60	6	8	76

TABLE III—(Continued)

Cylinder	Lg. cm	Outer diam. cm	Thickness of wall cm	Volume cc
I	26.0	0.11	0.02	0.25
II	23.0	0.18	0.02	0.50
III	4.2	0.53	0.04	1.20

Figure I shows the graphical representation of the values given in Table III.[1]

The most significant facts brought out by this figure are that the number of crystal nuclei is not proportional to the volume of the containing cylinder and that the maximum value for each curve comes at the same point on the temperature axis. In general, however, the number of centers is greater, the greater the volume of the liquid, as would naturally be expected.
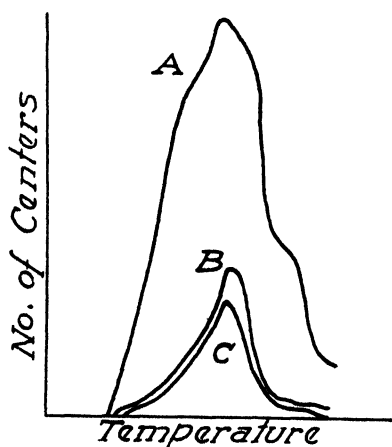
Fig. I

The second determining factor in the spontaneous crystallization of a supercooled liquid is the velocity of crystallization, or the speed with which the boundary between liquid and crystal is shifted. If the velocity is very small, centers might appear but they could not grow and the liquid would not crystallize. Piperin, for example, can be melted, then cooled until several centers appear and then if the temperature is lowered rapidly the centers remain the same size, and will not change until the temperature is again increased to a region where the velocity of cystallization is noticeable. To determine the velocity, the molten liquid is supercooled in a U-tube and inoculated at one end with a crystal nucleus. As time passes the crystal surface can be seen to grow. If

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[1] Tammann: Loc. cit.

crystallization velocity is plotted against temperature a diagram will be obtained similar to Figure II.[1]
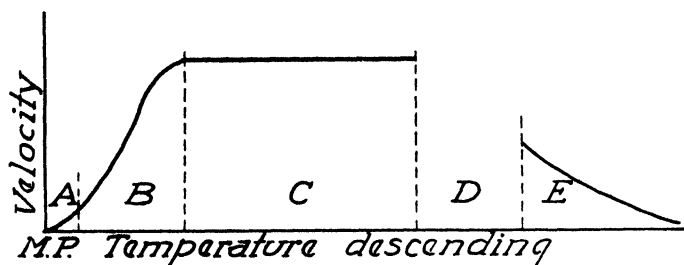
Fig. II

In considering this diagram three things must be borne in mind: (1) Bath temperatures are represented on the horizontal axis. (2) The temperature at the boundary layer between crystal and liquid is not the temperature of the bath, on account of the heat of crystallization. (3) When layers of liquid relatively far from the boundary layer are heated to the melting point, due to heat of crystallization, the velocity is high. If a thin layer only is heated to the melting point, the velocity will have a constant value as long as the heat of crystallization is sufficient to maintain this temperature in a thin layer. As the temperature at the boundary falls the velocity decreases still further.

At first, in range A, as the temperature of the bath is lowered, the values for velocity are small. The reason for this is that, owing to the insufficiently rapid removal of heat or crystallization, layers of liquid adjacent to the crystallizing boundary are heated to temperatures even above the melting point and the penetration of the crystal nuclei into these layers is retarded. In range B the velocity increases, in spite of the fact that the bath temperature is lower, since the heat of crystallization is sufficient to cause layers, that are far from the crystallizing layer, to be heated to the melting point. As the temperature of the bath decreases still further in range C, only enough heat is furnished to establish the melting

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[1] Tammann: Zeit. Elektrochemie, **10,** 532 (1904).

point temperature in a thin layer.   If the maximum velocity is less than 3 mm per minute, the heat liberated per unit of time is usually not sufficient to maintain the temperature of the melting point constantly at the boundary for an extended fall of temperature in the bath, and, in consequence, range C shrinks to a point.   Furthermore, with substances showing a rather high velocity the heat liberated will heat layers of liquid, still farther from the crystallizing boundary, as in range B, and the curve will continue to rise beyond C into range D.   In this range the velocity will rise to its maximum value.   Finally, in range E the heat of crystallization is no longer sufficient to establish the melting point temperature even in a thin layer, and the velocity decreases with increasing supercooling.

The viscosity is also related to the spontaneous power of crystallization and to the velocity, and its relation is brought out by the curves in Figure III.[1]

I = viscosity
II = spontaneous crystallizing power
III = velocity
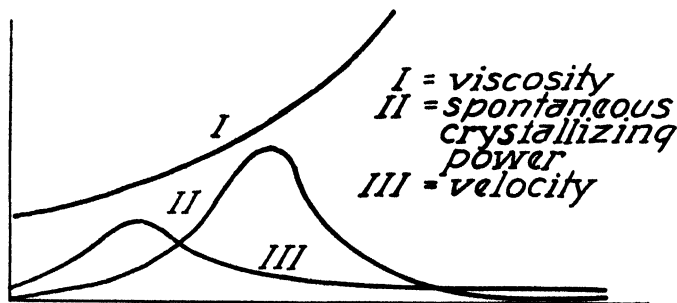
Fig. III

The viscosity of the liquid increases with descending temperature and frequently, in a small range of temperature, passes through all values from those of a syrupy liquid to those of a solid mass, and if the temperature is still further lowered· the mass becomes hard and brittle.   After passing the temperature range in which the maximum number of centers of crystallization are formed, the viscosity becomes very large and few, if any, centers appear in the brittle, glassy

[1] Tammann: Loc. cit.

mass. If centers did form they would not grow on account of the very small values of crystallization velocity in this region and the substance becomes highly stable, since the number of centers of crystallization is a measure of the instability of a supercooled liquid. The more there are, the greater is the tendency of the liquid to change its state of aggregation. A liquid can therefore be the more easily undercooled the fewer the nuclei in it, and the more slowly these nuclei grow.

Subject of Investigation

We undertook to ascertain experimentally the maximum degrees of supercooling obtainable in glass tubes with diameters varying from about one-half a centimeter down to the smallest we could conveniently manipulate. Our purpose was to settle the question as to whether supercooling could be more easily produced and could be carried further in capillary tubes than in larger tubes. Our hope was to find and establish some mathematical relation between the maximum supercooling effect and the diameter of the tube. And our intention was to include a number of different substances in the investigation.

At first the experiments were confined to a study of water as the supercooled liquid. Mixtures of ice and salt were employed as cooling agents, but they proved to be a source of annoyance due to the fact that the apparatus soon became encrusted with a layer of salt, which made it practically impossible to take readings on the thermometer immersed with the supercooled tubes. Solutions of solid carbon dioxide in ether or in alcohol were also used, as was a current of carbon dioxide gas escaping from a pressure tank and therefore cold, due to the expansion. The solutions, of course, evaporated rapidly and it became evident that the quantities we should have to use would involve too great a cost. We therefore abandoned, for the time at least, our originally planned work on water, and solutions in water, and turned our attention to materials whose melting points were between 100° and 125°. With these, all the cooling that was needed was obtained by

allowing the temperature of the bath containing the experimental tubes to fall gradually to that of the room. Almost all of the work was done with sulphur, oxalic acid, orthoacettoluid, β-naphthol and acetanilide. These substances were chosen because, with the exception of oxalic acid, they do not decompose at temperatures near their melting points.

Method and Apparatus

The material, enclosed in glass tubes immersed in a bath, was first heated to a temperature a few degrees above its melting point. It was held at this point until all had melted; the temperature was then allowed to fall and the temperature at which crystallization began in each tube was noted.

Along with each series of capillary tubes was included one large or standard tube. This tube was of sufficient diameter so that the enclosed mass represented a volume so large that the number of nuclei formed was considerable and the tube gave the smallest possible values for supercooling. This condition was fulfilled by tubes having diameters from 4 to 5 mm, which was smaller than we had anticipated. Numerous larger tubes were tried but none of them gave supercooling values different from those obtained with the 4 to 5 mm tubes. We then fixed, as it were, the upper limit above which the effects we were studying were not to be expected. Tubes of this dimension we called our standard or comparison tubes.

Ordinary soft glass tubing was steamed well to get rid of any soluble material and then left standing for several hours filled with the usual potassium bichromate-sulphuric acid cleaning mixture. It was then washed with distilled water, dried by drawing through it a current of air, and drawn down to the capillary sizes desired in the blast lamp. Suitable lengths of the capillary were then cut off with a small flame, thus sealing both ends. These little tubes were left sealed until we were ready to fill a series and start a set of observations. In filling the tubes the substance to be used was heated just above its melting point and held there until the whole mass

had melted. The tubes selected were opened, warmed and their ends were dipped into the liquid where they filled by capillary ascension. They were then removed and the substance, still liquid, was drawn up by suction into the tube far enough to allow the end to be sealed. The tubes were then reheated to a few degrees above the melting point of the substance in a bath and any leak could be detected by the ascension of bath liquid in that tube. Ordinarily, the length of the column of substance was only a few millimeters.

In order to regulate the rate of cooling, and in order to have normally a rather slow rate of cooling, it was found necessary to use a bath of from 600 cc to 800 cc capacity. A large beaker answered our purpose and an inner bath served to keep the temperature more nearly uniform for all the tubes contained within it. A variety of different liquids were tried in the bath but sulphuric acid was finally chosen in spite of certain risks of accidents thus entailed. The great advantage of sulphuric acid was that it could be used over a large range of temperature, but after repeated heatings it was found that it was satisfactory only for temperatures below 225 degrees. The bath was placed upon sand and an ordinary Bunsen burner was used for the heating.

After experimenting with several methods of stirring, a device was finally adopted which consisted of an inner bath of glass, a tube 3 cm in diameter and 22 cm long, closed at the lower end. The upper end projected through the center of a horizontal wooden wheel to which it was firmly attached. This wheel was supported on ball bearings and was rotated by an electric motor. Projecting almost to the bottom of the inner bath was a small glass tube which had attached to it, two platinum carriages. The capillary tubes, usually three or four in number, projected through openings in these carriages and were fastened at the top to the glass tube by means of an ordinary rubber band. The glass tube was fastened to a separate support and being stationary, while the inner bath was rotated, the arrangement effected the stirring.

A thermometer extended through the glass tube and its

mercury bulb was at the same level in the bath as the material enclosed in the capillary and standard tubes. The thermometers, ten inches long, were made especially for this work and have a scale about five inches in length on the lower half, while the upper half is left blank for purposes of fastening in position. In this way the whole scale was immersed in the liquid of the bath and no correction was necessary.   While this was not
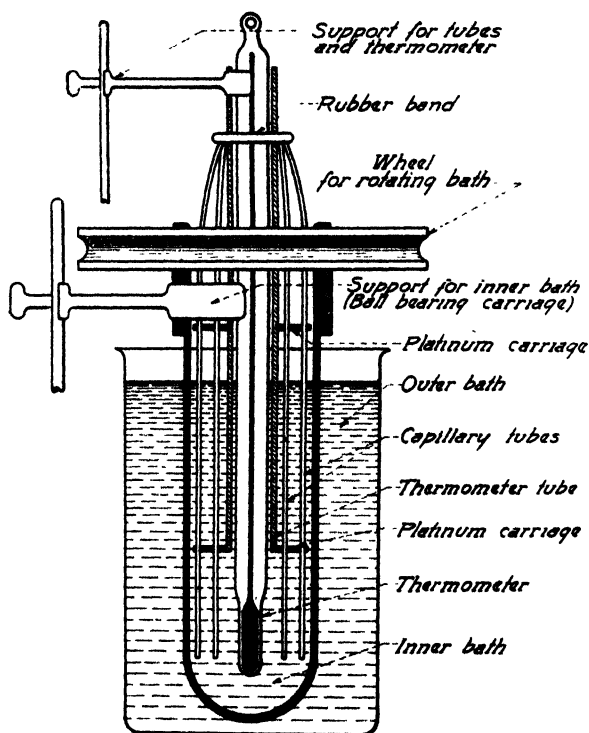
Fig. IV

important, the readings were much more easily followed where the whole scale was visible.   The scales were made in seventy-five degree lengths and each succeeding thermometer overlapped the one before by twenty-five degrees.   The thermometer, being removable, permitted the use of a wide range in temperature because one thermometer could be taken out and another covering a different range could be inserted.

The arrangement of tubes and thermometer is shown in Figure IV.

It was necessary to have an adjustable means for regulating the rate of cooling of the outside bath. A cooling coil of water was out of the question, since the cold coil, immersed in the acid at perhaps two hundred degrees, might break and under these conditions, explosions and serious accidents might result. A cooling coil of sulphuric acid was tried but was not found to be very efficient unless of a size so large that it would interfere with the readings. Finally a satisfactory method was devised by means of which cold sulphuric acid was added while the hot acid was simultaneously drawn off, thus keeping the bath at a constant level. By means of a suction flask and pump connected with a two-liter bottle, the hot acid was drawn through a glass tube at the top of the bath, passed through condensers for the purpose of cooling it and then was allowed to fall into a bottle. At the same time, by means of a pressure flask, cold acid was forced into the bath from a reservoir immersed in running water. For most substances this cooling was sufficient, but in cases where the substance had a low melting point it was necessary to keep the reservoir surrounded with a mixture of salt and ice. These two outfits were so connected that by turning several valves the cooled acid was drawn over into the reservoir and the process was ready to be repeated. Though the apparatus looked, and was, rather complicated it was very quickly and easily set in action or stopped. Figure V shows the arrangement.

In carrying out the experimental part of the work it was necessary first, to select a thermometer such that the melting point of the material enclosed in the tubes came near the top of its scale. Then supercooling values could be read on the same thermometer. In some cases the supercooling was so great that, in spite of this precaution, another thermometer covering a lower range had to be substituted later. The thermometer and tubes were adjusted as previously described and the temperature was gradually raised to a point not more
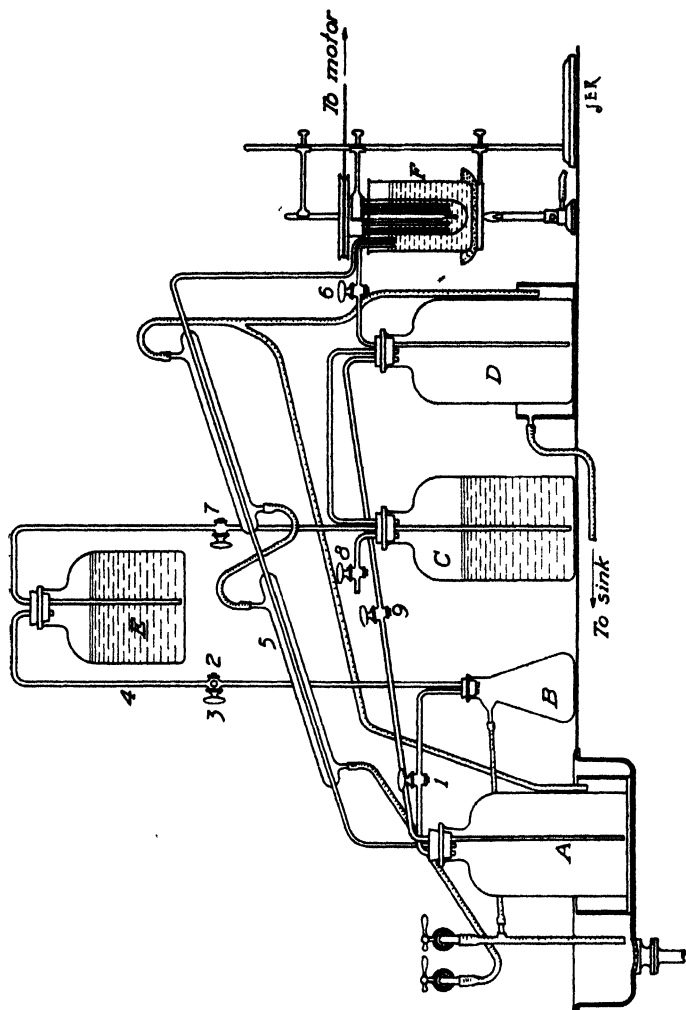
Fig. V

To Cool Bath: Open cock 1, close 9 and turn the three-way cock 3, closing it to 5 and leaving it open from 2 to 4.   Then the suction of the water pump draws the acid from the bath F through the condensers into the cooling bottle A.   At the same time leave cocks 6 and 7 open with 8 closed and water from reservoir E flows into pressure bottle C and causes the acid in D to pass through cock 6 into the bath.

To bring apparatus back to the original conditions: Close 1, turn cock 3 so that 4 is open to 5, close cock 6, open 9, open 7 leaving 8 closed and suction draws the acid back into D and at the same time draws the water from C into E. Cock 8 is to relieve the partial vacuum in C after the process is completed.

than five degrees above the melting point of the substance under investigation. With rapid heating the temperature of the inner bath lagged behind that of the outer bath, so, as the temperature of the outer bath approached the melting point, the rate of heating was gradually decreased. In this way it was possible to keep the temperature of heating from going more than five degrees above the melting point. The heating burner was then removed and the bath allowed to stand until the temperature had dropped several degrees. The cooling arrangement was then used to bring the bath down almost to the temperature which had been found by previous experiments to be the point where the material in the standard tube solidified. The bath was then allowed to cool more slowly, subject only to the cooler temperature of the room. A four-inch reading glass was used to magnify the smaller tubes so that the formation of the first nucleus could be noticed more readily. Immediately that this was seen, the temperature was read from the thermometer within the inner bath. The liquid of the bath also magnified the tubes within so there was no difficulty in making the required observation even with the smallest capillaries used. There was also no difficulty in noting when solidification began, since the transparent contents of a tube immediately became opaque, due to the solidified material enclosed. This procedure was repeated several times for each set of tubes and successive values of supercooling were obtained. After such a series of readings had been obtained the tubes were removed from the bath. The length of the column of confined material was then measured to tenths of a millimeter and the diameter in millimeters to three decimal places. The diameter was obtained by breaking the tube at a point where the material was enclosed and then inserting a short section of the tube vertically in a small clamp attached to a metal object plate. This plate was then put on the stage of a microscope and the inner diameter of the tube was measured by means of a calibrated scale in the ocular. A micrometer attachment allowed a hair to be moved across the field from one side of the tube to the other, the

movement being read directly by means of a calibrated drum on the ocular. The number of divisions on the drum multiplied by their actual value for the objective used gave the results in millimeters. Several readings were taken, as the cross sections of the tubes were not perfectly circular, and the mean value was recorded.

Results

The tables following give results obtained with some of the materials used. The data for all of our materials are not given, nor are all the data for a single substance shown. It is unnecessary to give more than we have given, since all results obtained were similar to those recorded. By degrees of supercooling is meant the temperature at which the first crystallization was observed, counting downward from the melting point of the substance. For instance, with sulphur, crystallization was first noted in tube 41 at 92° C. Then 114 — 92 = 22 degrees of supercooling.

The tubes are arranged in the tables in the order of increasing mean diameter. In all tables Lg. Col. = Length of

TABLE IV
Sulphur M. P. = 114-115° C

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3	S. C. 4	S. C. 5	S. C. 6
30	0.164	7.0	49.0	49.5	56.5	59.1	—	—
29	0.187	5.5	44.5	51.5	44.4	57.0	56.5	56.0
25	0.227	5.6	52.2	62.5	62.2	62.0	61.7	61.6
32	0.233	11.5	55.5	58.8	58.5	52.4	61.6	54.4
28	0.260	4.5	41.0	60.4	55.6	56.2	56.7	58.2
31	0.312	4.2	53.8	54.5	65.5	57.6	61.2	66.5
44	0.318	5.4	43.0	43.8	44.2	47.3	44.7	42.7
35	0.319	5.7	48.8	57.2	57.0	51.5	63.2	60.2
26	0.389	5.5	46.3	52.0	55.5	64.8	60.5	60.0
24	0.402	7.0	53.5	56.2	42.2	—	—	—
27	0.434	6.5	43.2	47.3	39.2	40.2	50.5	39.7
45	0.544	6.4	38.2	38.0	42.0	45.5	41.0	40.8
61	4.1	4.5	30.4	31.0	27.5	28.5	30.0	—
41	4.5	3.5	22.0	20.8	26.5	24.2	24.8	27.0

Column of material enclosed in tube; Mean Diam. = Mean Diameter of tubes; S. C. = Degrees of Supercooling; S. C. 1, S. C. 2, etc., represent values for successive heatings and coolings. Table IV contains some of the results obtained with sulphur.

TABLE V

Orthoacettoluid.   M. P. = 110° C

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3	S. C. 4	S. C. 5	S. C. 6
69	0.209	5.0	37.0	34.8	36.4	35.0	36.0	39.6
77	0.223	—	38.7	35.5	—	—	—	—
68	0.291	4.4	29.2	29.8	31.5	33.1	33.5	32.2
67	0.401	5.1	30.5	30.5	30.9	32.9	33.0	32.9
72	0.471	—	29.5	33.9	29.9	33.5	33.6	—
66	0.530	3.2	29.3	30.8	31.0	32.0	33.8	33.5
65	0.568	5.1	31.6	32.1	33.7	35.7	34.8	35.4
71	0.727	—	34.5	31.7	31.2	33.5	34.9	—
64	4.0	4.5	23.0	23.5	22.5	24.2	24.2	25.0
70	4.0	—	19.6	23.8	24.0	18.6	24.2	—

64 and 70 were the standard tubes.

TABLE VI

β-Naphthol.   M. P. = 122° C

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3	S. C. 4	S. C. 5	S. C. 6
80	0.327	4.2	16.8	18.0	17.0	16.6	17.8	19.2
91	0.342	5.1	11.8	13.3	16.2	13.2	—	—
83	0.353	4.0	14.7	16.0	14.1	17.5	18.2	17.4
79	0.382	4.0	14.5	15.0	16.7	16.7	18.5	16.0
82	0.394	5.0	10.5	16.4	13.0	16.3	18.6	17.3
90	0.409	9.5	14.0	13.2	16.0	16.0	—	—
81	0.420	11.0	13.0	13.0	14.5	16.2	16.2	16.3
89	0.459	5.2	15.8	15.7	18.3	16.7	—	—
88	0.499	4.1	15.7	15.6	16.1	16.3	—	—
87	0.672	2.5	14.7	14.0	15.5	16.8	—	—
86	0.695	3.2	15.3	18.4	17.5	17.5	—	—
85	4.3	4.1	6.5	5.6	5.4	6.0	—	—
84	4.3	4.0	5.5	4.5	4.5	4.5	5.2	5.5

84 and 85 were the standard tubes.

41 and 61 were the standard tubes and it can be seen that the supercooling was much less than with the capillary tubes. 35 and 44 were practically the same in size and yet there was a decided difference in the results. In this short table it looks as though 27 and 45, the largest of the capillary tubes, gave supercoolings that were consistently less than those of the smaller tubes, but these were exceptional cases, and later it will be seen that very small tubes give supercoolings no greater than those given by tubes of this size or even larger.

Table IV shows that it was impossible to obtain the same results in successive observations. This is equally true

<div align="center">TABLE VII
Acetanilide.   M. P. = 114° C</div>

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3	S. C. 4	S. C. 5	S. C. 6
131	0.174	5.6	46.6	47.8	42.5	47.3	—	—
123	0.182	5.5	48.0	48.0	—	—	—	—
129	0.189	6.5	47.6	46.7	47.2	47.0	—	—
130	0.203	4.5	47.7	46.7	46.8	47.4	—	—
126	0.206	7.2	47.7	47.4	46.6	45.6	—	—
128	0.213	5.4	45.3	47.5	46.8	46.9	—	—
132	0.234	4.4	46.6	40.5	43.6	44.6	—	—
127	0.248	4.5	45.2	46.5	45.8	45.3	—	—
120	0.249	2.4	47.0	47.7	—	—	—	—
121	0.249	5.8	47.6	43.7	—	—	—	—
122	0.264	4.3	46.9	46.0	—	—	—	—
125	0.285	1.8	47.6	47.5	46.5	45.2	—	—
117	0.328	5.1	46.0	45.4	—	—	—	—
114	0.433	3.3	42.9	45.3	45.1	45.6	44.7	—
118	0.336	3.2	46.8	47.6	—	—	—	—
119	0.336	4.0	45.0	46.0	—	—	—	—
116	0.353	4.5	46.1	45.5	—	—	—	—
113	0.405	3.1	44.7	46.0	45.0	45.0	46.0	—
112	0.409	4.0	44.0	45.2	43.9	44.1	44.6	—
110	0.466	2.5	43.8	45.3	45.1	44.7	46.0	—
108	0.575	5.1	43.1	43.1	43.6	44.2	44.0	—
111	0.677	1.8	—	43.0	41.0	41.9	43.4	—
109	0.698	4.5	38.7	38.7	39.8	42.0	38.8	—
115	4.3	5.0	37.5	37.5	—	—	—	—
124	4.8	6.5	36.7	33.0	36.4	38.4	—	—

115 and 124 were the standard tubes.

for the tables to follow. In some cases differences were very slight, but in many instances they were large. It is notoriously difficult to get concordant results upon supercooling, and bearing this in mind, it may be conceded, at least by those who have ever tried such experiments, that the results check better than might have been expected.

Here, although there was a wide range of tube diameter, the readings were almost the same in value. The smallest tubes gave, in some cases, equal supercooling or even smaller supercooling than the largest tubes, and we naturally expect them to give uniformly higher values in all cases. Here, also, a capillary tube 109 gave the same reading as the standard tube 124.

TABLE VIII

Oxalic Acid. M. P. = 98° C

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3
145	0.191	—	17.5	19.0	17.5
148	0.192	—	19.5	23.5	17.0
150	0.195	—	16.0	15.3	22.2
147	0.210	—	19.4	15.0	21.5
149	0.219	—	15.5	16.5	20.5
101	0.238	1.5	19.4	24.1	—
146	0.242	—	15.0	14.5	15.0
151	0.253	—	10.5	10.8	16.5
100	0.278	1.6	15.9	—	—
143	0.339	4.0	—	17.0	17.0
96	0.352	2.6	15.5	9.2	—
97	0.376	1.1	16.6	11.2	—
155	0.461	6.0	9.6	9.0	10.0
98	0.475	3.4	12.5	13.0	—
99	0.508	1.7	20.3	17.6	—
156	0.585	8.5	7.0	11.0	8.0
95	0.589	4.4	14.0	11.0	—
154	0.739	6.6	3.5	3.6	16.0
94	0.755	4.5	16.0	12.9	—
142	4.1	8.0	3.5	3.5	7.5
93	4.2	4.8	5.5	8.0	—

93 and 142 were the standard tubes.

Where the length of the column is not given it is because the thread of substance itself was broken into small segments due to the repeated heating. A column of from 4 mm to 6 mm in length sometimes broke up into as many as a dozen parts. This might have been caused by a slight decomposition of the acid as this splitting up was most pronounced with oxalic acid which loses its water of hydration just above its melting point. The substance was heated to only a few degrees above its melting point, just enough to make sure that all the material had melted. Sometimes the different fragments solidified at different temperatures, but usually they all crystallized out at the same time.

Here, again, some of the larger capillaries gave S. C. values almost as small as those found in the standard tubes 93 and 142. In tubes 145 to 151 columns of acid crystallized out at different temperatures, and on reheating these columns broke into a number of smaller segments, yet the results do not indicate that this further subdivision had much if any effect on the amount of supercooling. In some cases the readings were even higher than before, but as a rule the small segments gave values of supercooling practically the same as that obtained with the original column of material.

From a consideration of Tables IV to IX it is seen that, with very few exceptions, the contents of a standard tube solidified at a temperature above that at which the contents of the capillary tubes solidified. The difference, as a rule, was considerable, but comparing the results with the capillary tubes with each other, the amount of supercooling was not always the same for tubes of equal diameter, even when the length of the column was the same. The readings of the standard tubes did not always agree, but the differences here were much smaller than the difference between the results obtained in the capillary tubes. It is also evident that tubes of widely different diameters, but within what we may call capillary dimensions, gave practically the same readings. Comparing the capillary tubes with the standard tubes it is seen that the increase in supercooling is not proportional to

TABLE IX

Benzoic Acid.   M. P. = 121.4° C

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3	S. C. 4	S. C. 5
174	0.132	5.3	25.2	36.9	43.4	—	—
164	0.152	2.0	—	41.6	49.0	48.4	49.9
161	0.167	6.6	26.4	46.6	41.3	41.4	41.4
175	0.170	2.5	26.0	21.6	19.0	—	—
176	0.179	0.8	39.9	21.3	13.4	—	—
163	0.192	5.2	15.9	19.4	18.4	18.4	19.4
168	0.217	6.5	22.2	31.4	14.9	—	—
173	0.235	7.0	32.8	23.1	38.4	—	—
178	0.262	7.5	19.4	27.9	32.4	—	—
177	0.265	—	40.6	32.9	24.4	—	—
172	0.276	2.6	27.2	35.4	32.9	—	—
162	0.281	6.0	28.2	28.1	32.3	32.4	32.4
170	0.308	7.3	24.4	30.4	24.4	—	—
165	0.311	4.3	—	31.2	29.9	37.4	23.1
169	0.339	2.6	30.9	34.8	35.0	—	—
160	0.354	6.8	22.6	41.4	36.9	32.9	41.9
171	0.453	2.6	37.4	35.2	20.9	—	—
167	0.458	2.3	47.9	33.4	36.4	—	—
179	0.459	2.2	44.2	32.9	28.4	—	—
159	0.459	11.2	10.6	37.4	37.4	32.3	39.6
158	0.894	3.5	21.2	31.4	41.4	45.9	16.4
157	4.1	2.5	9.3	16.6	12.4	16.4	13.4
166	4.4	2.4	7.6	8.9	8.9	—	—

157 and 166 were the standard tubes.

the decrease in diameter.   It is also noticeable that the super-cooling is independent of the length of the enclosed column of material.

Interpretation of Results

It is reasonable to suppose that the arrangement of molecules making up a crystal nucleus is characteristic for every substance and that some internal molecular configuration or rearrangement is necessary in order that a nucleus may form.   It may be some such arrangement of the liquid molecules as given by A. Johnson[1] reasoning from the work of Laue and the Braggs on crystal structure.   According to

[1] Phys. Zeit., **16**, 269 (1915).

them, a crystal must have minimal symmetry; *i. e.*, must have one and only one of the 230 Schoenflies space groups, and at the same time it must conform with one of the 32 groups of symmetry. There must be some definite arrangement of the liquid molecules or atoms which, when the proper conditions are present, give rise to a crystal nucleus or center of crystallization. Now as the temperature of the substance is lowered below the melting point, crystallization takes place, but in materials such as we studied, the velocity of crystallization is such that the whole mass solidifies rapidly as soon as a single center appears. So when crystallization occurred in one of our tubes it denoted the temperature at which such a center first appeared. The molecules are in continuous motion within the liquid and no doubt many times assume the arrangement necessary for the formation of a center, but with small supercooling the viscosity is not great enough to retard the motion of the molecules and hold them in that position long enough for the centers to form and to allow the crystallization to begin. As the temperature decreases the viscosity is increased, thereby increasing the probability of crystallization until a maximum of probability is reached. Beyond this point the increased viscosity retards the formation of the centers or is so great that the internal rearrangement is hindered. Then if the temperature could be lowered enough without having a center form, the substance could be obtained in the form of a glass.

The number of centers formed spontaneously depends to a large extent upon the volume of the substance considered, and also upon the inclination of the curve obtained by plotting the number of crystal centers on one axis and the corresponding temperature on the other. See Figure VI.

If the number of centers increases rapidly with a decrease in temperature the conditions would be represented by curve X, but if the number of centers increases slowly with a decrease in temperature, curve Y would represent the conditions. Curve X could also represent the number of centers formed in a large volume, then curve Y would represent the conditions

in a small volume of the same substance. Since in a large
volume of a supercooled liquid the number of centers of crystal-
lization formed at any given temperature is greater than in
a small volume of the same material, the probability of a single
center being formed at the given temperature will be greater
in the large volume than in the small one.   That is to say, if,
in a certain volume there appeared four centers of crystalliza-
tion and in a smaller volume only one appeared, the proba-
bility of just one center forming would be four times as great
in the larger volume.   Let a point where such a center appears
be represented by A and A_1 on the curves in Figure VI. It
is seen that the number of centers formed at this temperature
is about four times greater in the case of curve X, or large
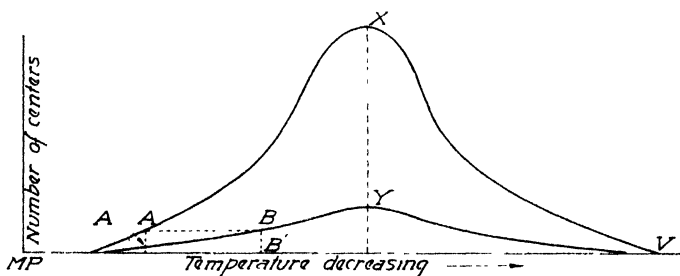
Fig. VI

volume curve, than for curve Y or curve of smaller volume.
In order to have equal probability for both cases it would
be necessary to pass along curve Y to point B.   Point B rep-
resents the same number of centers as point A, and hence the
probability of a single center forming would be the same.
But point B is at a much lower temperature than point A and
consequently, since all the materials used crystallized at the
appearance of the first center, the supercooling in the case of
the small volume would be much greater.   If the volume be-
came very small the probability might become so small that
not even one center would even appear and in this case the
liquid would remain uncrystallized.

    If, in the cases cited above, the number of centers was
very small even in a large volume, the temperature might be

lowered several degrees beyond the temperature indicated by the probability factor before crystallization would take place, or in other words, before a center would appear. The actual appearance of a center might then, as it were, lag behind the temperature at which we would expect it to appear. In a small volume, such as is represented by a capillary tube, the temperature might even be lowered ten or fifteen degrees beyond the point indicated by the probability value, before the material would solidify. This would allow a series of small, though unequal volumes, to give values of supercooling distributed all through this temperature interval and explains, perhaps, the range of equal readings obtained with capillary tubes of different diameters.

The fact that the supercooling was not proportional to the decrease in tube diameter, is in agreement with Tammann's observation, that the decrease in the number of crystal nuclei was much greater than the diminution in volume seemed to warrant, and it supports the connection that we have attempted to establish between the supercooling and the number of crystal nuclei.

That the supercooling was apparently independent of the length of the enclosed column of material seems to indicate that perhaps it is the shape of the supercooled volume and not the actual volume itself that is the determining factor. Perhaps the arrangement of the imaginary units of volume with respect to each other tends to aid or retard the formation of crystal nuclei. It is conceivable that a crystal nucleus, to form and to grow, needs to have some definite quantity of the substance all around it. Then for any volume, a spherical shape would give the largest number of possible centers, and any other would give fewer. In the discussion above then, perhaps the cross section of the various tubes should be considered rather than the corresponding volumes.

INFLUENCE OF VARIATION IN EXPERIMENTAL METHOD
Variation in Rate of Cooling

The number of crystal nuclei formed in a given mass is dependent upon the time, and from the relation established

between the number of crystal nuclei and supercooling (see Figure VI) we would expect to get greater supercooling under conditions of more rapid cooling. We found, however, that the rate of cooling made very little difference in the amount of supercooling obtained, as can be seen from the values given in Table X.

TABLE X

Sulphur   M. P. = 114–115° C

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3	S. C. 4	S. C. 5
61	4.10	4 5	32 5	31.5	27.9	28.0	27.7
62	0.917	6 0	45.0	43.0	45.5	53.3	48.5
63	0.214	6.5	50.8	52.0	52.5	54.0	53.6
Heated to			140°	140°	140°	140°	140°
Rate of Cooling			slow	slow	fast	fast	fast
61	4.10	4 5	34.5	36.2	41.0	36.5	47.0
62	0.917	6.0	49.5	55.8	46.5	46.5	52.5
63	0.214	6.5	58.9	61.7	66.0	61.4	62.0
Heated to			155°	155°	170°	170°	170°
Rate of Cooling			fast	slow	slow	slow	fast

Fast Cooling = about 5° per minute.
Slow Cooling = about 5° in 10 minutes.

The rate of cooling is not constant. At higher temperatures it is more rapid than at lower temperatures but the mean values above are close enough. The difference in supercooling under the different conditions of cooling from any one temperature was no greater than the difference in consecutive readings under the same cooling conditions.

Variation in the Material of Which the Tube Is Made

The point of solidification is mainly a function of the material itself, but there is a possibility of other factors influencing the crystallization to a certain extent. For example, different supercooling values might be obtained in tubes of glass and of platinum or contact with different substances might help or hinder supercooling. Some experiments were carried out to test this possibility, using acetanilide as the supercooled material. Two glass tubes of exactly the same

diameter and from the same piece of tubing, containing acetanilide, were heated in the ordinary manner and the solidifying point was noted. This was repeated several times in order to increase the reliability of our conclusions. Strands of glass and platinum were made of nearly the same diameter. The columns of acetanilide in the capillaries had been made of the same length. A piece of the glass thread was put in one tube and a piece of the platinum thread was put in the other, and they were long enough to pass through the acetanilide. The heating and cooling was then repeated in exactly the same way as before, both tubes being allowed to cool at the same rate.

TABLE XI
Acetanilide   M. P. = 112° C.   Heated to 120° C

Tube No.	Mean Diam. in mm	Lg. Col. in mm	Sub. Added	S. C. 1	S. C. 2	S. C. 3	S. C. 4
X	0.411	—	—	45.4	42.0	45.7	—
Y	0.411	—	—	45.3	45.2	44.8	—
X	0.411	5.2	Platinum	41.0	43.6	42.1	41.5
Y	0.411	5.2	Glass	41.7	44.8	44.0	43.5

Diameter of Strands—Platinum = 0.121 mm.   Glass = 0.116 mm.

The slight difference noted in the supercooling with the threads was practically the same as the difference between the successive readings of the tubes without them. These experiments led us to conclude that the nature of the surface in contact with the crystallizing liquid does not influence the temperature at which crystallization begins.

That a difference in the surface tension between the large and small tubes would account for the difference in supercooling hardly seems plausible since the difference in surface tension must be very slight. G. Quincke's[1] experiments seem to show that the difference between the surface tensions in tubes of different diameters is slight and that the surface tension is greater in larger tubes. The experiments

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[1] Wied. Ann., 52, 1–22 (1894).

of P. Volkmann,[1] however, indicate that the surface tension is smaller in larger tubes, but his experiments also show only slight differences between the surface tension values.

If in the tubes there were any relation between the surface tension and the supercooling obtainable, there ought to be some relation between the position of the center of crystallization and the surface. No such relationship could be found, the contents of the tubes beginning to solidify at times in the interior and at other times, perhaps, in the surface layer. If a change in the surface tension changed the amount of supercooling obtainable, it would be reasonable to expect a gradual, continuous change in the amount of the supercooling, increasing or decreasing as the diameters of the capillaries were varied. No evidence of this sort is perceptible in any of the tables. Some of the capillary tubes gave nearly the same values of supercooling as the standard tubes, while others of almost the same size gave much greater values.

PART II—EFFECT UPON THE SUPERCOOLING OF THE MOLECULAR AGGREGATION OF THE MATERIAL IN THE LIQUID STATE

Introduction

Since we believe that the formation of a crystal nucleus is due to a definite molecular configuration within the liquid, we would naturally expect to have a change in the character and number of nuclei if the molecular arrangement in the liquid were changed. This would undoubtedly involve a change in the supercooling values also. In fact, we could detect such a change in the liquid by observing changes in the values of supercooling. Such a transformation or rearrangement could be brought about in several ways but we shall confine ourselves to a study of the effect of variation in the temperature to which the material is heated. Sulphur has proved itself to be an ideal substance for this purpose and a review of the changes brought about in the liquid sulphur

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[1] Wied. Ann., **53** 633–663, 664–666 (1894).

by changes in temperature is necessary before our experimental results can be interpreted.

Chemistry of Molten Sulphur

The effect of the temperature to which liquid sulphur has been heated, has been the subject of a large amount of work. D. Gernez[1], by making use of the inoculation method for determining the freezing point, found that the freezing point of sulphur is not constant, but depends upon the temperature to which it has been heated. He found that when sulphur was fused at 121° C and cooled, the freezing point was 117.4°. When the liquid was heated to 144° it had a freezing point of 113.4° and when kept at 170° for five minutes the freezing point fell to 112.2°. Later he found[2] by heating sulphur to 160°, then allowing it to cool to 100° and holding it there for some time, that when the sides of the containing vessel were rubbed, a deposition of "pearly" sulphur was obtained. Smith and Carson[3] represented this pearly or nacreous formation by S_{III} orthorhombic by S_I and monoclinic by S_{II}. They found that the liquid from which the nacreous modification has been separated may be converted into monoclinic or orthorhombic sulphur by the touch of a corresponding crystal. In the conversion of liquid to ordinary crystals in this way, the reaction takes place with seven-fold rapidity after the nacreous crystals have been deposited, and Gernez considers that at the temperature of 160° the allotropic pearly modification is produced, and by its solution in the rest of the liquid the latter is in the condition of a supersaturated solution. F. W. Küster[1] found that the amount of insoluble sulphur present after solidification was dependent only upon the rate of crystallization and the temperature at which the crystallization occurred, and not upon the temperature to which it had been heated nor upon the length of time of heating. He concludes that the soluble and insoluble forms of

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[1] Comptes rendus, **82**, 1151 (1876); Phil. Mag., [5] **2**, 79 (1876).
[2] Comptus rendus, **98**, 144 (1884).
[3] Zeit. phys. Chem., **71**, 661–676 (1911).
[4] Zeit. anorg. Chem., **18**, 365 (1898).

sulphur are isomerides. Other experimenters, however, seem to agree that the insoluble variety of sulphur is present in increasing amounts as the temperature is raised above the melting point. P. Duhem[1] explains the difference in velocity of crystallization of sulphur as due to the difference in concentration of the insoluble form. Alexander Smith[2] found that the formation of insoluble sulphur takes place in an irregular manner as the temperature is raised above the melting point and that the depression of the freezing point is proportional to the amount of insoluble sulphur thus formed. In a later investigation[3] he found that yellow mobile sulphur (S_λ) predominates from the melting point to $160°$ and that the brown viscous or amorphous (insoluble) sulphur (S_μ) increases greatly in amount above $160°$ at the expense of S_λ. He thought that this indicated a transition point, since a separation into the two phases, yellow and brown liquid sulphur, was observed.[4] Later, however, he[5] accepted the view of Hoffman and Rothe[6] that there is no transition point in the ordinary sense, for if the rate of cooling was diminished the discontinuity did not appear and therefore the two modifications must, under ordinary conditions, be completely miscible with each other. The apparent separation into two phases was brought about by the differences in temperature which arise in a column of the liquid owing to the poor conduction of heat, in reality there being no formation of two phases, the difference in color being accounted for by the difference in temperature. Smits and Leuw[7] apparently accepted these views also since they found that the liquid sulphur contains the two forms S_λ and S_μ in equilibrium proportions.

[1] Zeit. phys. Chem., **23**, 193–266 (1897).

[2] Ibid., **42**, 469 (1903); Proc. Roy. Soc. Edin., **24**, 299, 342 (1902).

[3] Proc. Roy. Soc. Edin., **25**, 588 (1905).

[4] Jour. Am. Chem. Soc., **27**, 797–820 (1905).

[5] Proc. Roy. Soc. Edin., **26**, 352 (1906); Zeit. phys. Chem., **59**, 448 (1907); Jour. Am. Chem. Soc., **29**, 499 (1907).

[6] Zeit. phys. Chem., **55**, 113–124 (1906).

[7] Proc. Akad. Wetensch. Amsterdam, **14**, 461 (1911); Zeit. phys. Chem., **83**, 221–241 (1913).

In addition to S_λ and S_μ, A. H. Aten[1] has described two other forms of sulphur, S_π and S_ϕ. S_ϕ is not formed, however, by the action of heat upon sulphur and is of no interest to us. S_π is formed when sulphur is heated above its melting point and then is rapidly cooled. The relative quantities of S_λ, S_μ and S_π present in sulphur which has been heated to various temperatures have been determined by Aten.[2] The amount of S_π is at a maximum when the sulphur has been heated to 180° and at this point the amount present is 6.5%. The quantity of S_μ increases as the temperature rises to 448° C, the greatest rate of increase being between 170° and 180°. S_λ decreases as the temperature increases. He gives the composition at 180° as S_π = 6.5 percent, S_μ = 20.4 percent and S_λ = 73.1 percent.

Summarizing all this: when sulphur is heated to various temperatures above its melting point there are present principally the four modification S_γ, S_μ, S_π and S_{III}. S_λ is soluble sulphur and is present in the greatest amounts, decreasing, however, with increase of temperature above the melting point. S_μ is insoluble or amorphous sulphur which increases in amount as the temperature is raised with the maximum rate of increase between 170° C and 180°. S_π is present in small amounts but increases to a maximum as the temperature is raised to 180° and then decreases. S_{III} or pearly sulphur, begins to form at 160° C. The various forms of sulphur occurring together in the liquid state are mutually miscible.

Influence of Foreign Material upon the Formation of Crystallization Nuclei

Tammann[3] has observed that the addition of soluble materials to a supercooled liquid causes a decided change in the number of crystal centers and in the temperature at which a maximum number forms per unit time. By the addition of one substance the temperature for maximum number of

[1] Zeit. phys. Chem., **81**, 257–280 (1912); **88**, 321–379 (1914).

[2] Ibid., **86**, 1–35 (1913).

[3] Ibid., **25** 453 (1898).

centers was lowered while the addition of another substance would cause a shift towards higher temperatures. In some cases the maximum point was at the same temperature but the number of centers was changed, with some added materials the number being larger, and with others, it was smaller. Of course this caused a decided change in the slope of the curve. We have indicated the relation between the number of crystal nuclei and supercooling and have also shown the effect of the slope of the curve representing the variation in number of crystal centers with temperature. It would seem, then, that added foreign materials would cause a change in supercooling, either increasing it or decreasing it as the case may be.

As sulphur is heated to various temperatures above its melting point, increasing amounts of new and in that sense foreign materials are formed as has just been described, consequently a shifting of the curve representing the number of crystal nuclei could be expected. Since the amount of supercooling in capillary tubes depends upon the position of the maximum and the slope of the nuclei curve, any such shifting would be indicated by a change in the amount of supercooling obtained.

Method and Results

The degrees of supercooling of sulphur when cooled from temperatures just above its melting point have been given. When it was heated to points between 120° and 200°, changes in the supercooling values with the capillary tubes were observed. The heating was carried on in the usual way. Both rapid and slow cooling was tried with no noticeable difference in the results. Table XII shows the effect of heating to different temperatures upon the amount of supercooling afterward obtained, and it also shows that whether the cooling is fast or slow the results are practically the same.

In obtaining the results given in Table XII the tubes were first allowed to cool slowly from the temperature given in the table and then the time of cooling was shortened for the same tubes from the same temperature point. The fast cooling was about 12° per minute while the slow cooling

TABLE XII

Sulphur   M. P. = 114–115° C

Cool = Rate of Cooling   Heat = Temperature to which Substance
was heated

Tube No.	Mean Diam. in mm	Lg. Col. in mm
61	4.10	4.5
62	0.917	6.0
63	0.214	6.5

Tube No.	S. C. 1	S. C. 2	S. C. 3	S. C. 4	S. C. 5
61	30.4	31.0	27.5	28.5	30.0
62	36.0	47.0	47.3	46.5	50.2
63	37.8	41.5	54.4	42.5	53.0
Cool	slow	slow	slow	slow	fast
Heat	125°	125°	125°	125°	125°
61	32.5	31.5	27.9	28.0	27.7
62	45.0	43.0	45.5	53.3	48.5
63	50.8	52.0	52.5	54.0	53.6
Cool	slow	slow	fast	fast	fast
Heat	140°	140°	140°	140°	140°
61	34.5	36.2			
62	49.5	55.8			
63	58.9	61.7			
Cool	fast	slow			
Heat	155°	155°			

Tube No.	S. C. 1	S. C. 2	S. C. 3	S. C. 4	S. C. 5	S. C. 6	S. C. 7	S. C. 8
61	34.0	34.5	37.0	43.5	44.2	42.0	46.0	44.5
62	45.5	44.5	45.5	51.0	50.5	45.5	50.5	56.0
63	93.0	92.5	80.0	66.0	86.0	80.0	76.0	80.0
Cool	slow	slow	slow	fast	fast	fast	fast	fast
Heat	170°	170°	170°	170°	170°	170°	170°	170°

Tube No.	S. C. 1	S. C. 2	Tube No.	S. C. 1	S. C. 2
61	38.3	41.0	61	33.5	42.0
62	48.0	48.0	62	48.0	56.2
63	75.0	75.5	63	59.5	66.2
Cool	slow	fast	Cool	slow	fast
Heat	190°	190°	Heat	225°	225°

Tube No.	S. C. 1	S. C. 2	Tube No.	S. C. 1
61	41.0	36.5	61	47.0
62	46.5	46.5	62	52.5
63	60.0	61.4	63	62.0
Cool	slow	slow	Cool	fast
Heat	170°	170°	Heat	225°

was about 1.2° to 2° per minute. This was repeated at each successive elevation of the temperature to which the heating was carried, but as can be seen from the table, no great change in the supercooling was observed. At about 170° a decided change was noticed in the readings with the smallest tube 63. The largest tube 61 did not show such a large change and the intermediate tube 62 gave values between those of the other two. Tubes of practically the same diameter gave wide variations, as subsequent data will show, but as a rule the values of supercooling were larger than those given by this tube 62. When the heating was carried to about 225°, smaller values were again obtained which persisted even when the tubes were reheated to 170°, the temperature corresponding to the maximum supercooling. It may be inferred that the modification which formed at 170° was permanent since a tube heated to that temperature and cooled gave the same value when reheated to 125° and cooled at the same rate.

With the ordinary supercooling of sulphur from its melting point the whole mass solidified in an instant as soon as the first center appeared, but where the supercooling was carried to room temperature before a center appeared the rate of crystallization was decidedly slow and the solidification of the mass continued to grow from the first center formed while the temperature was lowered perhaps ten degrees in five minutes. The fact that no more centers formed even when the tube was so slowly cooled through ten degrees, seems to point to a small number of centers even at the maximum point.

A graphical representation of the data in Table XII is given in Fig. VII. The horizontal axis represents the de-

grees of supercooling and the vertical axis shows the tempera-
ture to which the heating was carried before the supercooling
was measured.   Points on the curves represent average values.
Although Curve B crosses Curve C at the lowest preheating
temperature used, it is evident that it follows the contour of
the curve for the standard tube for its whole length, and this
might be expected since the tube is hardly of capillary di-
ameter.
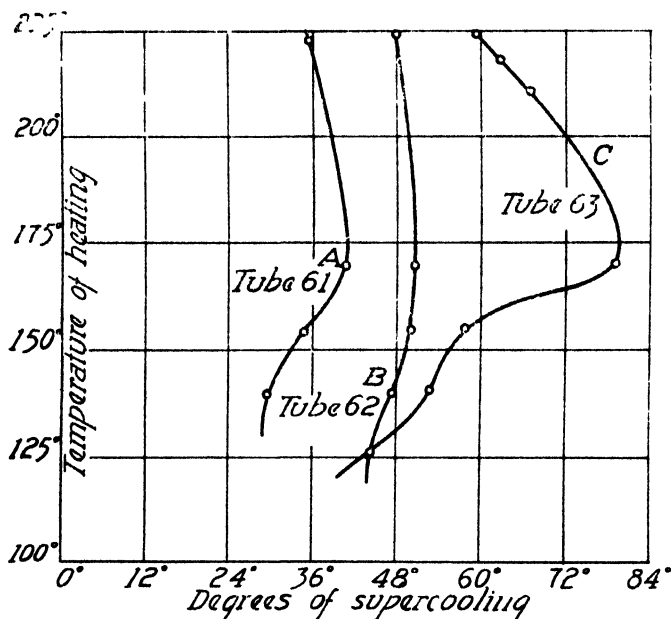
Fig. VII

In order to show that the change at 170° was permanent
a series of capillary tubes were heated to 170°, then cooled
to 100° and held there for five hours.   The supercooling
values were then determined and they corresponded to those
obtained without this long wait, instead of to those obtained
after heating only to a lower temperature.   The tubes were
again heated to 170° and this time cooled to 75° and held at
this temperature for several hours.   The results were similar

to those obtained when the wait was at 100°. If the change within the liquid had not been permanent it would surely have reversed itself to at least some extent, during these long waits. The experimentally observed values are given in Table XIII.

TABLE XIII

Sulphur

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3	S. C. 4
219	0.191	5.6	55.0	64.0	51.0	58.7
222	0.205	4.3	55.5	87.5	83.0	78.5
218	0.211	4.2	43.8	70.0	72.5	73.7
217	0.237	5.2	44.0	88.0	71.0	75.9
214	0.252	5.5	44.0	59.4	59.0	56.3
213	0.267	5.7	59.0	83.0	81.0	79.0
215	0.271	6.5	53.0	64.5	76.5	77.5
216	0.276	5.2	48.0	78.5	70.5	71.0
212	0.321	3.9	41.0	48.5	70.8	74.0
211	0.339	4.8	47.0	56.0	58.0	55.0
210	0.429	3.5	50.7	—	71.0	69.0
Temp. heated to			125°	185°	185°	185°

After the readings S. C. 2 were taken, the sulphur was heated to 185°. It was then cooled to 100° and held at this point for five hours and then cooled as usual giving the readings in S. C. 3. This procedure was repeated for the values in the column headed S. C. 4 except that the temperature was first lowered to 75° and held here for five hours. It was then cooled as usual giving the readings in S. C. 4.

Table XIV gives more data of the same kind as that in Table XIII and confirms further our belief that holding the temperature constant at a point far below the temperature where we presume a permanent transformation took place, is without effect in reversing the transformation.

TABLE XIV
Sulphur

Tube No.	Mean Diam. in mm	Lg. Col. in mm	S. C. 1	S. C. 2	S. C. 3
206	0.201	4.7	84.5	91.0	100.0
201	0.220	5.6	68.5	58.0	55.0
205	0.238	5.8	68.0	82.5	81.5
204	0.272	3.5	69.0	83.0	89.2
203	0.281	4.0	88.5	74.0	95.5
202	0.284	4.0	59.0	64.0	82.0
198	0.470	8.2	68.0	64.5	73.0
199	0.655	5.4	67.0	62.0	60.0
Temp. heated to			$190°$	$185°$	$185°$

After the readings S. C. 2 were taken the sulphur was heated to 185°. It was then cooled to 100° and held at this point for three hours and then cooled as usual, giving the readings in S. C. 3.

Interpretation of Results

The greatly increased supercooling obtained with capillary tubes after heating to 170° or above indicates a broad shifting of the crystallization center curve towards lower temperatures. The probable change is indicated in Fig. VIII.
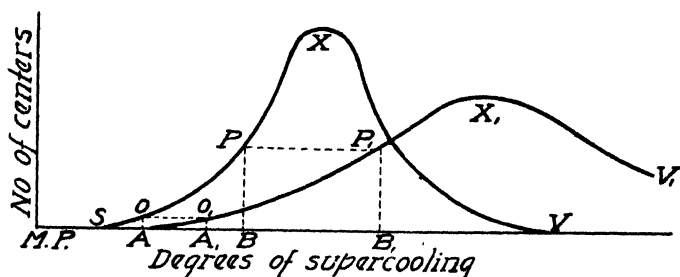
Fig. VIII

The effect of added materials upon the position and character of the nuclei curve has already been discussed. In Fig. VIII the added materials are the various forms of sulphur formed by the action of heat at temperatures above the melting point. Curve X represents the conditions in liquid

sulphur which has been heated only to the melting point and Curve X_1 represents conditions resulting from heating to 170° C. The two curves start to leave the horizontal axis at approximately the same point since the change in supercooling values for the standard tube is very small. As has been said, in a large volume such as in a standard tube, a center of crystallization will appear practically as soon as suitable conditions are present, and this would be where the curve starts to leave the temperature axis. The maximum value for Curve X_1 is below that for Curve X since we have found that the number of centers formed in sulphur that has been heated to 170° is smaller than when it is heated only to the melting point. The maximum point will also be farther along the temperature axis for Curve X_1 since the increase in supercooling for the capillary tubes is very large. With a lower maximum point shifted to the right, Curve X_1 will have a more gentle slope than Curve X.

The point of crystallization for the standard tubes is represented by O and O_1 the projections of which upon the horizontal axis give the temperature readings A and A_1. P represents the point where sulphur in a capillary tube, that has been heated only to the melting point, will crystallize out, the increased elevation of the point counterbalancing the decreased volume. Thus P and O would represent equal probability of crystallization. Point P_1 represents the crystallization point for the same tube after it has been heated to 170°. Equal elevation for the same volume indicates equal probability for the formation of a crystal nucleus. But in the case of P_1 the temperature is lower, which corresponds to greater supercooling.

Let us assume that S_μ and S_τ have a combined effect in shifting the curve of crystal centers to the right in Fig. VIII. The increase in supercooling indicated by the gradual rise of Curve C in Fig. VII would then be attributed to the gradual formation of S_μ and S_τ. In the neighborhood of 160° the rate of formation of S_μ suddenly increases and this is indicated by the bend in the curve at S continuing to V. The influence

of S_r now grows less since the maximum percentage comes at 170° and simultaneously S_{III} or nacreous sulphur is formed. If we assume that the addition of S_{III} to the fused mass causes the curve to shift in the same direction as does S_μ and S_r then there will be no decided break in the curve but the curve will continue to rise more gradually to the right, the increasing amounts of S_{III} partially making up for the decreased rate of formation of S_μ and S_r. Apparently, however, S_{III} at temperatures above 170° exerts an opposite and stronger effect than does S_μ for there is a sharp bend in the curve at 170° and above this temperature it gradually approaches the vertical axis. The corresponding Curve A for the standard tube shows the same effect but less pronounced.

Conclusions

We have designed a form of apparatus for the measurement of supercooling in capillary tubes.

We have shown that decidedly greater supercooling can be produced in capillary tubes than in tubes of larger diameter.

We did not succeed in formulating a mathematical connection between the amount of supercooling obtainable and the diameter of the capillary.

We have developed a plausible explanation for the increase in supercooling found possible in capillary tubes.

We have obtained evidence indicating that the material of the tube has little if any effect on the degree of supercooling, and have reached the conclusion that small changes in surface tension are likewise of insignificant importance.

We have found that in the case of sulphur, the amount of supercooling depends upon the temperature to which the substance was heated previously.

We have offered a plausible explanation of this interesting phenomenon.

SATURATED SOLUTIONS OF POTASSIUM AND MAGNESIUM SULPHATES AT 25° C

BY H. S. VAN KLOOSTER

Van't Hoff, in giving an exposé of the work done by himself and his collaborators on the formation of oceanic salt deposits, discusses also the case of the polyhalite paragenesis at 25° C.[1] Polyhalite [$Ca_2MgK_2(SO_4)_4.2H_2O$], first artificially prepared by Basch,[2] coexists at 25° C in stable equilibrium with either two of the three composing salts syngenite [$CaK_2(SO_4)_2.H_2O$], reichardtite [$MgSO_4.7H_2O$] and gypsum [$CaSO_4.2H_2O$] in solutions of potassium magnesium sulphate (the calcium sulphate being practically insoluble herein) of different, though adjacent, compositions. This being the case, the question arises, and was actually put by van't Hoff[3] whether there does not exist a temperature, not far from 25° C, below which polyhalite should break into the three salts above mentioned. Exactly at this temperature, polyhalite would coexist with three salts in equilibrium with a solution, the composition of which was to be found out. This was the starting point of the present investigation. On repeating the experiments of Basch and finding not inappreciable deviations from his results, I thought it not inadvisable to redetermine carefully the solubility-curve of potassium magnesium sulphate solutions at 25° C in order to test, first of all, the existing data by Basch and others. The determinations were carried out in a large water-bath, kept at constant temperature (25° C) by means of two thermoregulators, the fluctuations in temperature amounting to ±0.1° C, and exceptionally (during the night) to ±0.2°. Special care was taken that before each determination the temperature remained at least one hour at exactly 25° C. The components potassium sulphate (K_2SO_4), magnesium sulphate ($MgSO_4.$-

[1] Zur Bildung der ozeanischen Salzablagerungen II, p. 21 (1909).
[2] Diss. Berlin 1901. Darstellung und Bildungsverhältnisse des Polyhalits.
[3] Loc. cit., p. 21.

7H₂O) and water were brought together in Erlenmeyer flasks
of 100 cc, closed by cork stoppers, which turned with moderate
speed about an axis, moved by a Henrici gas motor. The
time of shaking varied from 3 to 10 days, although saturation
will generally be reached in the course of a day. The potas-
sium sulphate was purified by recrystallization, the mag-
nesium sulphate was the purest product from Kahlbaum
(*pro analysi*). The solutions were analyzed by evaporating
the water and determining the dry residue, the magnesium
sulphate was weighed as pyrophosphate ($Mg_2P_2O_7$) [method
of Gibbs, cf. Treadwell, II, p. 59 (1913)], the percentage of
potassium sulphate was found by subtraction. The experi-
mental data are given in the table below and graphically ex-
pressed in Fig. 1, where—following van't Hoff's representa-
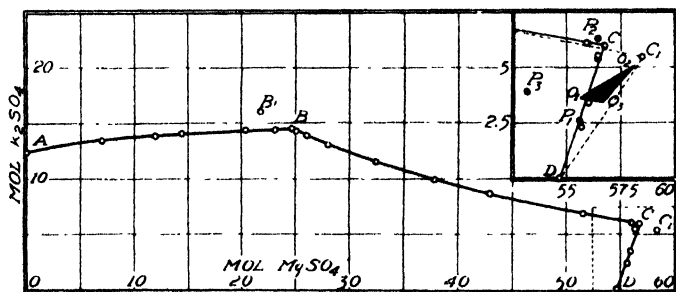
Fig. 1

tion—the abscissae represent the number of molecules of
$MgSO_4$ in a thousand molecules of water and the ordinates
the corresponding figures for K_2SO_4. The point A, repre-
senting the solubility of K_2SO_4 at 25° C, gives 12.5 mol
K_2SO_4 in 1000 mol H_2O, equal to 12.07 parts of K_2SO_4 in
100 parts of water in accordance with the careful determina-
tions of Trevor[1] and Meyerhoffer,[2] who found 12.04 and 12.06,
respectively. In B, saturation of potassium sulphate and
schönite exists, expressed by 14.5 mol K_2SO_4 and 24.8 mol

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[1] Zeit. phys. Chem., **7**, 470 (1891).
[2] Landolt and Börnstein's Tabellen, 3rd Ed , p. 547 (1905).

TABLE I

Saturated solution	Time of shaking in days	Residue after evaporation in %		MgSO₄ determined in %		K₂SO₄ by substraction in %	Molec. MgSO₄ on 1000 mol H₂O	Molec. K₂SO₄ on 1000 mol H₂O
			Average		Average			
A	4	10.76 10.78	10.77	—		10.77	—	12.5
AB	5	15.05 15.02	15.03	3.96 4.03	4.00	11.03	7.0	13.4
AB	6	17.62 17.57	17.60	6.64 —		10.96	12.1	13.8
AB	7	18.89 18.91	18.90	7 83 7.76	7.80	11.10	14.4	14.1
AB	8	21.48 21 58	21.53	10.67 10.70	10.69	10.84	20.4	14.3
AB	5	22.83 22.82	22.83	12.07 12.04	12.06	10.77	23.2	14.4
B	3	23.37 23.39	23.38	— 12.68		10.70	24.8	14.5
BC	7	23.44 23.36 23.38 23 38	23.39	12 83 12 89 12.91 —	12.88	10.51	25.1	14.3
	10							
BC	6	23 58 23 61	23.60	13.23 13.29	13.26	10.34	26.0	14.0
BC	5	23.89 23.91	23.90	14.30 14.23	14.27	9.63	28.1	13.1
BC	5	24.80 24.77	24.79	16.36 16.36	16.36	8.43	32.5	11.6
BC	5	25.96 25 95	25.96	18.80 18 72	18.76	7.20	37.9	10.0
BC	9	27.05 27 01	27.03	20.86 —		6.17	42.8	8.7
BC	7	29.13 29 15	29.14	24.44 —		4.70	51.6	6.9
BC	4	30 23		26.12		4.11	56.0	6.1
C	6	30.41 30.41 30.40 —	30.41	26.35 26.42 26.48 26.32	26.39	4.02	56.7	6.0
	3							
CD	6	30.10 30 11 30.10 30.18	30.12	— — 26.40 26.32	26.36	3.76	56.4	5.5
	10							
CD	—	29.90 30.00	29.95	26.50 26.30	26.40	3.55	56.4	5.4
CD	8	28.91 28.89 28.93	28.91	26.57 26.56	26.57	2.34	55.9	3.4
CD	—	28.35		26.67		1.68	55.7	2.4
D	—	26.76		26.76		—	54.7	—

MgSO$_4$, whereas the corresponding data given by van't Hoff are 16 and 22 (point B$_1$), probably derived from determinations made by Precht and Wittgen[1] in 1882. Saturation of schönite and reichardtite (MgSO$_4$.7H$_2$O) is reached in C (6 mol K$_2$SO$_4$ and 56.7 mol MgSO$_4$); the point C$_1$ (*viz.* van't Hoff, l. c., p. 30) derived from Basch's determinations is represented by 5.3 mol K$_2$SO$_4$ and 58.3 mol MgSO$_4$. The solubility of MgSO$_4$.7H$_2$O (point D) was found to be 54.7 mol, differing but slightly from the value given by Basch (54.8 mol). As will be seen from the figure, the Curve AB is slightly convex, BC is distinctly concave, whereas CD does not differ essentially from a right line. Part of the figure, limited by the dotted lines, in the right corner is represented also on a larger scale, to give a better idea of the discrepancies, found in repeating the experiments of Basch, carried out with the purpose to continue his work in the direction outlined by van't Hoff (l. c., p. 31) as described above.

Now the points O$_1$, O$_2$ and O$_3$ represent—according to Basch—solutions of potassium magnesium sulphate, in equilibrium, respectively, with

1. Polyhalite, reichardtite and gypsum,
2. Polyhalite, reichardtite and syngenite,
3. Polyhalite, syngenite and gypsum,

with the following composition:

O$_1$ = 3.6 mol K$_2$SO$_4$ and 55.7 mol MgSO$_4$ ⎫
O$_2$ = 5.1 mol K$_2$SO$_4$ and 58.1 mol MgSO$_4$ ⎬ in 1000 mol H$_2$O
O$_3$ = 3.5 mol K$_2$SO$_4$ and 56.7 mol MgSO$_4$ ⎭

All three points lie *within* the field limited by DC$_1$ and C$_1$B, so that these solutions ought to be unsaturated in regard to K$_2$SO$_4$ and MgSO$_4$.7H$_2$O. In preparing these solutions, however, I found that only the composition O$_1$ gave a complete solution, whereas O$_2$ left some salt (MgSO$_4$.7H$_2$O) undissolved, and O$_3$ still more, a sure indication that C was rightly determined.

After having prepared and analyzed the required salts

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[1] Ber. deutsch. chem. Ges., **15**, 1666 (1882).

polyhalite and syngenite[1] (reichardtite and gypsum being present in pure state), 50 cc of the solutions O_1, O_2 and O_3 (O_1 unsaturated, O_2 and O_3 saturated, as shown above) were brought together with the required salts in excess (at least 5 grams) and shaken during several days in the thermostat, taking care that after each period of shaking a period of rest followed, because there are indications (*viz.*, van't Hoff, l. c., p. 21) that equilibrium is sometimes delayed by shaking. The results were as follows, Table 2:

<div align="center">TABLE 2</div>

Saturated solution	Time of shaking in days	Time of resting in days	Dry residue one in %	MgSO₄ determined in %	Mol MgSO₄ in 1000 mol H₂O	Mol K₂SO₄ in 1000 mol H₂O
			Average	Average		
Solution O_1	7	2	28.41	—		
The same again	2	4	28.33 / 28.28 / 28.39 } 28.35	26.65 / 26.59 / 26.68 } 26.64	55.6	2.6 (point P_1)
New mixture, same comp.	8	2	28.33	26.64		
Solution O_2	—	—	29.69	—	—	—
			29.76	26.23		
The same again	7	2	30.43 / 30.46 / 30.45 / 30.40 } 30.44	— / 26.20 / 26.22 / — } 26.21*	56.4	6.3 (point P_2)
The same again	5	1				
Solution O_3	7	7	28.26 / 28.22 } 28.24	25.50 / —	53.2	3.9 (point P_3)

* K_2SO_4 by difference 4.23%. A direct determination, after Treadwell II, p. 366, by eliminating the Mg gave 4.12% K_2SO_4.

A comparison of these data with those of Basch (l. c.) shows that for solution O_1, instead of a dry residue of 28.91

H. S. van Klooster

percent and a quantity of 26.45 percent $MgSO_4$, are found, respectively, 28.35 percent and 26.64 percent (solution P_1). Instead of 30.45 percent and 27.01 percent (solution O_2), the corresponding results (solution P_2) are 30.44 percent and 26.21 percent. Practically the same value for the dry residue is found, whereas there is a difference of not less than 0.8 percent for the $MgSO_4$ present in the solution. In the case of solution O_3, Basch gives 29.22 percent and 26.80 percent, differing largely from the corresponding values (solution P_3): 28.24 percent and 25.50, albeit that in the latter case only one experiment was made, so that there was no proof of any state of equilibrium being reached.

The discrepancy between my results and those of Basch is too great to be attributed to errors of analysis. Most probably his way of experimenting was not the suitable one, so that no real equilibrium was reached. Consequently the conclusions of van't Hoff based on them seem to be very questionable. In bringing the results, so far obtained, to the notice of those interested in work on salt solutions, I only wish to call attention to some inaccurate data in this field of research, brought to light by the present investigation.

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   Easton, Pa.

NEW BOOKS

Lubricating Engineer's Handbook. *By John R. Battle. 23 × 17 cm; pp. 333. Philadelphia: J. B. Lippincott Company, 1916. Price: $4.00 net.*—In the preface the author points out that the importance of the almost limitless field of lubricating engineering may be appreciated from the fact that not a spindle can turn without overheating and wear, nor can the largest locomotive in the world move a heavy train, unless there is a lubricant provided to reduce the ever-present friction between the bearing surfaces. The headings of the chapters are: friction, theory of lubrication; historical (petroleum); petroleum and other lubricants and greases; lubricating oil and grease tests; oil data and miscellaneous notes; mechanical and engineering data; steam engines and steam turbines; electrical engineering data; rolling and sliding friction, and its application to bearings; the lubrication of steam cylinders; oil cups, grease cups, and filters; oil-houses and oil-house methods; the steam engine indicator and its use; air compressors and their lubrication; automobile lubrication; coal mining machinery lubrication; Diesel engines; the lubrication of baking machinery, dough dividers; the lubrication of electric street cars and interurban electric cars; the lubrication of passenger and freight elevators; flour milling machinery; refrigerating and ice-making machinery; internal combustion engines (explosive type); marine engines and marine oils; motors and dynamos and their lubrication; newspaper printing machinery and operation; the lubrication of pneumatic tools; the lubrication of railway locomotives and cars; rolling mills and their lubrication, textile machinery, operations and lubrication; transformers and transformer oils; steam turbines and their lubrication, water-wheel generators; wire drawing and its lubrication; the cost of lubrication; specifications.

Although the book is written primarily for lubricating engineers, there are a number of things in it which are of general interest, as for instance on pp. 23, 25, 93, 188, 190, 216, 289, 299, and elsewhere.

"To obtain the least fractional resistance between a rotating journal and its bearing, it is necessary that the rotating part be 'floated' by a film of lubricant, so that there will be no metallic contact between the surfaces. The sliding layer theory is based on the assumption that the lubricating film is split into two or more layers due to the adhesive action between the lubricant and the metallic surfaces of the journal and bearing, which is greater than the cohesive attraction between the particles composing the lubricant. Part of the layers, therefore, revolve relatively to the rotating journal, and the remaining layers tend to remain at rest, as is the surface of the bearing, so that a sliding movement takes place between the layers of the lubricating film. Since the frictional resistance between the oil layers is small, the frictional resistance of the bearing is reduced."

"The running clearance of the ordinary engine main bearing is only about 0.005 of an inch for a six-inch to a twelve-inch shaft. When the shaft revolves and the lubricating film is broken into several layers, it can readily be appreciated that the thickness of the individual layers must be very thin. The cohesive action within the layers is not strong enough, due to their thinness, to produce very much of an effect towards surface tension. We must, therefore, consider that it is the cohesive resistance to tear, within the body of the lubricating layers, rather

than the increased elasticity of the surface of the layers, that is the deciding factor in the maintenance of the lubricating film. A good lubricant must possess the proper proportions of the properties of cohesion and adhesion in order that it may have the greatest efficiency. An excess of either is unsatisfactory. Mercury has an excess of cohesion and very little adhesion. Water has an excess of adhesion and a low proportion of cohesion. It is obvious that neither of these fluids would be satisfactory as a lubricant.

"The ideal lubricant for any bearing must possess just enough viscosity to enable it to maintain a lubricating film through all the conditions and requirements made upon it. It should not, however, have any excess of viscosity at normal air temperatures or at the normal running bearing temperatures, since the internal friction of the lubricant is directly proportional to its viscosity. Therefore, to avoid an unnecessary friction load, use an oil having as low a viscosity at stationary and at running bearing temperatures as will maintain the lubricating film. It is possible to increase the friction load of a bearing 25 percent by increasing the viscosity of the lubricant."

"Oil used as a lubricant creeps over the outer surfaces of a bearing, even at ordinary temperatures, due to the fact that air is drawn into oil, by the rotative action of the journal and due to the rapid flow of the oil in the feed pipes. This air spreads through the body of the oil in the form of finely divided bubbles. These bubbles burst when they come to the surface and form a fine spray, which settles on the exterior of the bearing, causing a waste of oil."

"Road dust, metallic wear, or too rich a mixture of gasoline, are the usual causes of the so-called 'carbon deposits,' which are usually blamed unjustly upon the lubricating oil. There will always be some carbon deposit formed in the cylinders of an internal-combustion engine, but it should be of such a nature that it will largely be removed with the exhaust. An excess of oil in the crank-case will cause 'carbon deposit' troubles. The level of the oil should never be carried above the height indicated by the oil gauge. Too high a level will cause the oil to work up past the piston rings into the explosion space. Here the oil is partially burned and deposits will result. Chemical analysis of many 'carbon deposits' has indicated that about 70 percent of these so-called 'carbon deposits' found in the cylinders of automobiles consist of mineral matter. The analyses of these deposits show a large percentage of undecomposed oil, a small percentage of decomposed oil, a little free carbon, and, as before stated, about 60–70 percent mineral matter. The mineral matter is hard and abrasive and causes wear between the piston rings and the cylinders. It is introduced into the cylinders during the suction stroke of the piston, which sucks in dust from the road mixed with the air, and which eventually gets into the crank-case, where it is mixed with the oil and then is worked up into the cylinders. The heat of the explosions hardens the deposit, forming a 'carbon-appearing scale.' A small projection of this hard scale, remaining in the upper part of the cylinders, may become overheated and retain enough heat to ignite the incoming gas during the charging stroke. This condition is indicated by a pounding noise in the cylinder."

"It has been stated by some investigators that motor oils manufactured from paraffine base crudes give a more objectionable carbon deposit in the cylinder than is produced by the oils made from asphaltic base crudes. A careful working test to investigate this statement has indicated that the amount

of carbon found in automobile engine cylinders averages the same, for high or
low viscosity oils made from either paraffine of asphaltic base crudes. The
consistency of all motor cylinder 'carbon deposits' is about the same, irrespec-
tive of the source of the oil. The amount of carbon deposit produced depends
upon the amount of oil actually reaching the upper part of the cylinder."

"In the past it was believed that lubricating oil for use in the cylinders
of internal-combustion engines should possess a high flashing-point, to prevent
its destruction during the firing stroke. This theory has been given up for the
following reason. In order to obtain a flashing-point of over 500° Fahr., with
a petroleum oil, it is necessary to use a cylinder stock oil, with all of the resulting
disadvantages of slow distribution of the lubricant, due to its high viscosity at
normal and even fairly high temperatures The average working temperatures
in the cylinders of internal-combustion engines are far above 500° or even 600°
Fahr., so that even a high test oil will be burnt with practically as much rapidity
as an oil having only 400° Fahr. flash test and a much lower viscosity. It has
been demonstrated by many practical tests, that the most important character-
istic of an oil, in the lubrication of internal-combustion engine cylinders, is its
viscosity The viscosity should be as low as practicable, to permit of a quick
and efficient 'spread' of the oil over the cylinder walls The flashing-point of
the oil is of minor importance.

"Due to the fact that the same oil is used for both the cylinders and the
bearings of internal-combustion engines of the light high-speed type, now in
most general use in automobiles, motor-boats, etc., it is desirable, and the best
lubricating efficiency can only be secured, by using an oil having a viscosity, at
the average running temperatures of the bearings, that is just sufficient to meet
the physical operating conditions of these bearings, so that the distribution of
this same oil over the surfaces of the cylinder walls will be accomplished with
speed and effectiveness and not retarded by an unnecessarily high viscosity.
The following theoretical discussion illustrates the fact that the outer part
of the lubricating oil film, when exposed to the hot gases during the firing stroke,
protects the inner part of the film, which remains upon the cylinder walls It is
important, therefore, to replace this outer film quickly with fresh oil after the
firing stroke, which demands a free-flowing, low viscosity oil The bearings
are heated by conduction, through the metal of the connecting rods, etc , and the
oil is compelled to work under high bearing temperatures The viscosity of the
oil should be sufficiently high to allow for a reduction, due to the bearing tempera-
tures.

"Due to the high rubbing speeds of the piston, the period of time, during
which the lubricating film is exposed to the high temperatures of the firing stroke,
is very short. The maximum temperatures usually met with in the cylinders
of internal-combustion engines are usually about 2700° Fahr. This is the max-
imum temperature for the cylinder gases, and the temperature range will proba-
bly run as low as 250° Fahr., thus giving a mean temperature of the gases, for
the complete cycle, of about 950° Fahr.

"A film of petroleum oil, if exposed to a high temperature as described
above, will not be burnt instantly, but will require that it be exposed to this high
temperature for an appreciable length of time before it will be destroyed. It
must, therefore, be assumed that in the cylinders of these engines the high speeds

and loss of heat in its transmission to the lubricating film, will result only in partial destruction of the lubricating film. There will be, therefore, a partially destroyed film of lubricant remaining upon the walls of the cylinders after the firing stroke has been expended. It is the heat conditions, to which this remaining film is exposed, that determine the severest requirements made on the lubricant, because this film remains on the walls of the cylinder, which are hot, for a longer time than the outer film is exposed to the hot gases. While the cylinder walls are at a lower temperature than the hot gases, the increased time of exposure of the inner film to their heat causes the lubricating film, as a whole, to be attacked on the hot gas side by high temperatures for a short period of time, and, on the cylinder wall side, by lower temperatures for a longer period of time.

· "The value of the outer film as a heat-protecting blanket for the inner film may be compared relatively as follows: In a paper read before the Institute of Naval Architects in England, it was stated that a film of lubricant one one-hundredth of an inch thick, a layer of boiler scale one-tenth of an inch thick, and a steel boiler plate 10 inches thick, offer equal resistance to the passage of heat."

"An important factor in the lubrication of drawing iron wire is the lime coat. When the rods first come to the wire mill they are covered with scale. This scale must be removed, as its hard surface would destroy the die hole. To accomplish the removal of this scale, the rods are immersed in hot, diluted sulphuric acid, which dissolves and loosens it. A stream of water is then run on the rod bundles and the loosened scale washed off. The rods are next immersed in a hot lime-water vat and a thin lime coating adheres to them. This coating is believed by wire manufacturers to have great value in aiding the lubrication of the metal as it is drawn through the dies. It is not known whether the lime combines with the grease to aid it in lubrication, or whether the roughened surfaces merely aid in carrying an increased quantity of the lubricant into the die. The lime-coated rods are baked before being taken to the wire benches."

"It has generally been taken for granted in the past that the lubricant applied to tools during the cutting operation flowed between the edge of the cutting tool and the work. If the enormous pressure which is required at the cutting edge of the tool, and which often exceeds 100,000 pounds per square inch, is compared with the maximum pressure of even 1000 pounds per square inch, which a lubricant of as light a viscosity as that required for cutting-tool lubrication must have, it can be readily appreciated that the lubricant does not form a film between the tool edge and the work. When metal is cut, there is a large amount of heat generated. This heat is produced by the slipping of the metal chip over the surface of the tool, by the separation of the chip or cut from the metal body, and by the 'crimping' of the cut. * * * * Sharp tools are only possible when the heat of cutting is removed at a sufficiently high rate, by the lubricant, to prevent the overheating and drawing of the temper of the high carbon steel used to make these tools. * * * * Of all liquids available for the 'lubrication' or cooling of the cutting operation, water has the highest heat-absorbing qualities. It can also be readily flowed into contact with the heated surfaces, but, due to its low viscosity, will not form a satisfactory lubricating film for the sliding of the chip over the face or lip of the tool. The rusting properties of water make it unsuitable as a cutting lubricant when used alone.

Petroleum oil, cottonseed oil, and lard oil have the required body to form the necessary film on the tool lip, and, while their specific heats or heat-absorbing properties are only about half as high as water, they have the property of preventing rusting. The usual soluble cutting oil is made of a combination of oils as outlined above, and is designed to permit its being mixed with varing amounts of water to form a stable, cutting emulsion. The amounts of water required vary with the character of the work. For tough steel, a larger amount of water is used than for the more brittle metals, since the steel chips press against the face of the tool with greater force and for a longer distance."

In regard to specifications the author says, p. 297: "The crude oil conditions are constantly changing, and therefore a specification calling for a certain viscosity and gravity may allow competitive bidding from many oil companies this year; then, due to a falling off in the production of certain fields and the increased production in other fields, the specifications may quickly become obsolete and limit the number of competitors for the business in succeeding years. The gravity and the other characteristics may call for an oil from a particular field in which the conditions have materially changed. The result is an increased price for the oil, or restricted bidding. In preparing specifications, some particular oil must be used as a sample. Specifications written on tests from the sample limit the source of the crude from which the specification oil can be made. This may be desired, but such a condition prevents receiving the benefit of the constant improvements which are being made by the different lubricating oil manufacturers in the oils made from the various crudes. If specifications are desired, they should not be too closely written. Their purpose should be to secure a satisfactory oil for fulfilling certain conditions, at the lowest competitive prices, and should not be written with the view of excluding oils made from crudes, other than that of the tested sample. An exactly stated gravity, viscosity, and flash will pin all bidders to very narrow limits. Gravity is of no importance. Lubrication depends upon viscosity and its characteristic variations."

Wilder D. Bancroft

The Respiratory Exchange of Animals and Man. *By August Krogh. 24 × 16 cm: pp. viii + 173. New York: Longmans, Green & Co., 1916. Price: $1.80 net.*—In the preface the author says: "The subject of the respiratory exchange of animals is not one of physiological chemistry but rather of chemical physiology. It deals with very few substances, and with their quantities, not qualities. The relations between respiratory exchange and functional activity have been excluded from the scope of the present monograph, which deals therefore with one very limited problem only: the quantitative aspect of the catabolic activity of the living organism as living. To give an exhaustive account of the work done even in this restricted field has not been attempted; but I have endeavored to trace out the essential lines of study, to state the fundamental problems, and to indicate the solutions of them so far as such solutions appear to have been reached—with what amount of success it is for the reader to judge."

The subject is presented under the headings: the physiological significance of the exchange of oxygen and carbon dioxide; methods for measuring the respiratory exchange; the exchange of nitrogen, hydrogen, methane, ammonia, and other gases of minor importance; definition and determination of the stand-

ard metabolism of the organism; the influence of internal factors upon the standard metabolism; the influence of chemical factors upon the respiratory exchange; the variations in standard metabolism during the life cycle of the individual; the respiratory exchange in different animals.

The respiratory exchange of an animal in the widest sense of the term means the exchange of gaseous substances taking place between the organism and the surrounding atmosphere. It is not defined by any physiological difference between the part played within the body by these substances and others, but solely by practical considerations of convenience. The respiratory exchange in the strict sense of the term comprises only the oxygen intake and the elimination of carbon dioxide. When dealing with individuals of the same species, it seems probable that the gas exchange should be calculated per unit surface and not per unit weight, pp. 113, 133. It has been shown that men of the same size and weight may differ considerably with regard to their standard metabolism. The results vary from 2.8 cc oxygen absorbed per kilogram and minute to 5.5 cc, or from about 0.8 Cal. per kilogram and hour to 1.6 Cal. The differences are to be ascribed in many cases to differences in the proportion of fat in the body, as the fatty tissues appear to have only a very slight metabolism. Fat persons have also been found experimentally to have a smaller respiratory exchange than lean ones. The value 5.5 cc oxygen per kilogram and minute (= 1.6 Cal. per kilogram and hour), which is very unusual, was obtained by Caspari on a trained athlete, and recently Benedict and Smith have compared a number of athletes with 'normal' subjects of similar height and weight, and have shown that the metabolism of athletes is on an average distinctly greater than that of non-athletes (1.083 Cal. per kilogran and hour as against 1.017).

Wilder D. Bancroft

Analytical Chemistry. *By F. P. Treadwell. Fourth English Edition translated and revised from the Eighth German Edition by William T. Hall. Vol. I. Qualitative Analysis. 23 × 16 cm; pp. xiii + 538. New York: John Wiley and Sons, 1916. Price: $3.00 net.*—This text on Qualitative Analysis furnishes an admirable companion book for the excellent text on quantitative analysis by the same authors. It strikes a happy medium between the ponderous reference text and the too abbreviated laboratory manual. The theoretical part covers 76 pages, the reactions of the common cations 207 pages, the reactions of the rarer elements 60 pages, the reactions of the anions 137 pages, and systematic analysis 32 pages. The theoretical portion, in addition to the discussion of such topics as properly apply to Qualitative Analysis, contains valuable tables of solubility products and oxidation potentials. The brief paragraphs on occurrence and general properties, which precede the detailed discussion of each cation and anion, are a pleasing feature. *G. E. F. Lundell*

THE RADIOACTIVITY OF PHILIPPINE WATERS

BY J. R. WRIGHT AND GEORGE W. HEISE

In recent years there have been so many investigations of the radioactivity of waters that comparative data are now available from many different parts of the world. It is the purpose of this paper to present the results of similar work on the radioactivity of typical Philippine waters.

Up to the present time our work on radioactivity has been limited to the determination of radium emanation and actual radium content of typical springs and deep, drilled wells. As yet, no attempt has been made to study the radioactivity of the deposits or residues from springs, or of typical rocks, or of the gases evolved from springs or wells. All of the work was done on Luzon, part of it at high altitudes in the mineral-bearing mountainous region and the remainder practically at sea level.

Owing to the difficulties of travel, equipment for provincial expeditions had to be reduced to a minimum; in consequence comparatively few data on the chemical composition of the waters were secured.

Experimental Part

The testing apparatus was a Spindler and Hoyer aluminum leaf electroscope used in previous radioactive measurements[1] in the Philippines. The instrument was provided with the usual equipment of tripod, shaking vessel, and circulation system necessary for field work.

Owing to the high humidity generally encountered in the Philippines, a small tube of calcium chloride was fastened inside the leaf chamber of the electroscope. In all determinations, in the field or in the laboratory, a calcium chloride tube (generally of the Bender and Hobein type) was introduced into the circulation system, so that all air and gases were

[1] J. R. Wright and O. F. Smith: Phys. Zeit., 15, 31–39 (1914); Philippine Jour. Sci., 9A, 51–77 (1914); Phys. Rev., 5, 459–482 (1915); 7, 49–61 (1916).

dried before they entered the ionization chamber. It was found impossible to obtain reliable readings without this precaution. Our results indicate that drying is also necessary at lower temperatures in order to ensure correct results with the type of instrument used. With the precautions noted, the natural leak was usually lower in laboratory work, and frequently lower in field work, than the figures for the natural leak furnished by the instrument makers. The electroscope was charged by means of a bank of storage cells in the laboratory; in the field, by means of an ebonite rod.

The electroscope was standardized by means of a radium bromide solution of known strength secured[1] from the Bureau of Standards, Washington, D. C. A definite portion of this solution was kept sealed in a proper vessel (essentially a "Curie[2] tube") for over one month. The emanation was then removed from the solution by boiling and by circulation of air and drawn into the evacuated ionization chamber.

The standardization was checked with a known quantity of standard radium bromide solution put directly into the shaking vessel used in field determinations. After the closed vessel had been allowed to stand one month to ensure radioactive equilibrium, a determination was made by the usual field method. Two different determinations showed satisfactory agreement with each other and with the results previously obtained. This procedure is much simpler than the usual method of standardization, and since determinations both with the standard solution and with water samples of unknown activity are thus performed under identical conditions, the chance for error is minimized. Our data indicate that this method can be relied upon for accurate results.

The shaking apparatus of Schmidt[3] was employed in field

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[1] Our thanks are due the Bureau of Standards, Washington, D. C., for the standard radium solution used in this work.

[2] P. Curie: "Dosage du radium par la mesure de l'emanation dégagée," LeRadium, **7**, 65–70 (1910).

[3] H. W. Schmidt: "Uber eine einfache Methode zur Messung des Emanationsgehaltes von Flüssigkeiten," Phys. Zeit., **6**, 561–566 (1905).

work. Determinations were made as soon as practicable after a sample had been taken; usually within thirty minutes and in no case after more than three hours.

Samples of typical waters were brought to the laboratory, sealed up in proper vessels, allowed to stand for one month, and tested for radium content. Instead of Curie tubes, 400 cc Jena flasks, equipped with aspirator tubes, were used to hold the water. About 250 cc of water were used in a determination. In some cases, when larger quantities of water were available, as much as 15 liters were evaporated to 250 cc, acidified with hydrochloric acid, sealed up in Jena flasks, and tested.

Though the object of this work was primarily to get reliable comparative data rather than exceedingly accurate absolute values, it is probable that the error was not great. The radium solution used for standardization may be considered accurate within 5 percent. Duplicate determinations made with the standard solution checked within 1.5 percent. Duplicate determinations made in the field on the same water checked within the limits of observation error. We have reason to believe that, except for isolated cases in which proper samples could not be secured because of the nature of the source, the maximum error in field determinations was not greater than 7 percent. The probable error was, therefore, much smaller and hence was well within the limits of accuracy to be expected for this class of work.

No attempt was made in the field to determine anything but radium emanation content. That we were actually dealing with radium emanation was shown by the fact that when the gases from a number of the waters studied were allowed to remain in the ionization chamber for long periods of time the typical decay curve of radium emanation was obtained.

The radioactivity of over ninety Philippine waters was determined, the following data being typical:

TABLE I—RADIOACTIVITY OF PHILIPPINE WATERS. (SOURCES DESIGNATED BY * HAVE REPUTATIONS FOR MEDICINAL OR HEALING PROPERTIES)

No.	Date 1916	Location (Province, town, and barrio)	Source	Geological formation[1]	Radium emanation[2] Curies per liter × 10^12	Remarks
1	June 7	Batangas, Batangas	Artesian well	—	2106	Non-thermal
2	June 6	Batangas, Batangas	Crater lake, Taal volcano	Volcanic sinter	³	—
3	April 9	Bulacan, San Miguel de Mayumo, Sibul Springs	Sibul Springs*	Limestone	1284	Non-thermal mildly sulphuretted
4	June 9	Bulacan, San Miguel de Mayumo, Sibul Springs	Sibul Springs*	Limestone	1293	Non-thermal mildly sulphuretted
5	June 20	Laguna, Calamba Pansol	"Pansol" Springs*	Volcanic basalt	Neg.	Series of large hot and cold springs Sample from cool portion (31° C)
6	June 11	Laguna, Calamba Pansol	"Pansol" Springs*	Volcanic basalt	Neg.	Sample from hot portion (45° C)
7	April 19	Laguna, Los Baños	Hot Spring,* near sanitarium	Igneous conglomerate cemented by tuff	539	Temperature 70° C; probably from same source as water for sanitarium
8	June 29	Laguna, Majayjay. Olla	"Olla" spring	Loose volcanic agglomerate	528	Temperature 22° C; probably (see page 531) from a river in vicinity
9	June 29	Laguna, Majayjay, Malinoa	"Sinabac" spring	Igneous conglomerate	1297	Temperature 25° C
10	June 24	Laguna, Nagcarlan	"San Diego" spring*	Igneous conglomerate	526	Temperature 25° C
11	June 21	Laguna, Pagsanjan, Maulauin	Small artesian well	—	880	Temperature 32° C
12	June 21	Laguna, Pagsanjan, Pinagsanjan	"Bumbungan" spring*	—	146	Temperature 31° C
13	June 30	Laguna, Pakil	Spring "Baño"	Igneous conglomerate	365	Temperature 25.5° C
14	June 22	Laguna, San Pablo	Spring "Bañadero"	—	713	Non-thermal
15	June 22	Laguna, San Pablo, Maganpun	Spring "Baño"	—	606	Non-thermal
16	June 22	Laguna, San Pablo, Santa Maria	Spring "Años"	—	324	Temperature about 40° C. Located in bed of river Añosai; sample probably mixed with river water

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17	June 22	Laguna, Santa Cruz	Large artesian well, No. 459	—	Nil	Temperature 36° C
18	May 30	La Union, San Fernando	Municipal spring	Andesite	242	Non-thermal
19	June 1	La Union, Santo Tomas	Artesian well*	—	Trace	Non-thermal
20	April 29	Mountain, Baguio	Camp John Hay No. 1 spring	Igneous, fined grained rock	194	Non-thermal; supplies Camp Hay, elevation about 3,500 ft.
21	April 29	Mountain, Banaue	Small spring near school house	—	381	Non-thermal; elevation 3,400 ft.
22	May 14	Mountain, Bontoc	Spring adjacent to municipal spring	Volcanic tuff	Neg.	Non-thermal, elevation about 2,800 ft.
23	May 10	Mountain, Cervantes	Hot spring on river bank. opposite town	—	Nil	Temperature 50° C; elevation about 2,400 ft.
24	Dec. 18	Mountain, Itogon	Hot springs*	Andesite	Nil	Temperature 45°
25	Dec. 18	Mountain, Kiangan	Spring E. of school, on Nueva Viscaya road	—	1058	Non-thermal; elevation about 2,700 ft.
26	May 29	Mountain, Klondike	Klondike springs*	Igneous conglomerate cemented by tuff	Trace	Temperature 50° C; elevation about 600 ft.
27	May 15	Mountain, Mainit	"Mainit" spring*	Andesite siliceous and calcareous sinter	Nil	Sample from boiling saline spring, elevation 4,000 ft.
28	May 8	Mountain, Mancayan	Spring on Balili trail	Trachyte andesite	114	Non-thermal, elevation about 4,700 ft.
29	May 12	Mountain, Sagada, Tetepan	Small spring at slide	Decomposed andesite	263	Elevation 4,000 feet
30	May 31	Mountain, Sagada, Tetepan	Artesian well, calle Espanol	—	137	Temperature about 35° C
31	June 19	Rizal, Parañaque	Artesian well, plaza	—	632	Temperature about 35° C

[1] Most of the data in this column were furnished by V. E. Lednicky, Chief, Division of Mines, Bureau of Science.

[2] If there was no change in the leak when radioscope was filled with gas, emanation content is designated as "nil;" when increase was so slight that its magnitude was uncertain, emanation content is designated as "neg" ("negligible"); when increase was positive, but too small to warrant calculation, emanation content is designated as "trace."

[3] Tested for radium content only. Negative results with 250 cc.

In order to examine waters for actual radium content, 250 cc samples of twenty typical waters, from which the emanation had been removed, were acidified, sealed up in proper containers, and allowed to stand at least one month. In no case was there any indication of radioactivity at the end of that time.

In addition, 15 liters of Batangas water (No. 1), 15 liters of Los Baños water (No. 7), and 5 liters of Sibul Springs water (No. 3) were evaporated to small bulk and similarly tested. The first two showed no emanation, and the third showed a trace.

The radioactivity of the waters studied, therefore, was due primarily to emanation derived from the materials in the ground with which the water had been in contact.

Discussion of Results

The work has not proceeded sufficiently to justify many conclusions. The typical Philippine water supplies studied possess no abnormal features, so far as their radioactivity is concerned. Though some of them are moderately high in radium emanation content, none show an excessive amount, compared with waters from other countries reported in the literature.[1]

Since hot water is a poorer solvent of gases than cold water, it is to be expected that the radioactivity of hot springs should, in general, be low. With the exception of the Los Baños water (No. 7), most of the thermal waters studied in the course of this work showed little or no activity.[2]

In general, the average activity of igneous rocks is greater than that of the sedimentary,[3] and it is to be expected that water from the former material should show the higher emana-

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[1] Cf. Schlundt and Moore: Bull. U. S. Geol. Surv., **395,** 29 (1909); Jour. Phys. Chem., **18,** 662 (1914); D. Isitani: Proc. Tokyo Math. Physic. Soc. (1912), ff., etc.

[2] The average temperature of Philippine ground waters in the lowlands is about 28° C.

[3] Cf. F. W. Clarke: "Data of Geochemistry," Bull. U. S. Geol. Surv., **166,** 122 (1916).

tion content. Thus Sahlbom[1] found that the water from sedimentary deposits was much lower in activity than that from primary rocks; further, that wells bored in the acid rocks showed the highest activity. In the Philippines the relatively small number of determinations made and the frequent difficulty of determining the actual water-bearing stratum, since this is frequently not the same as the geological formation exposed at the place where the water emerges, make generalizations at this time inadvisable.

In some cases at least, the radioactive material from which the water derived its activity must have been confined to a rather limited area. Thus it was pointed out[2] that "Olla" Springs (No. 8) were in reality only seepage water derived from a river about a hundred meters distant. The "spring" water must obviously have acquired its activity in the course of a short journey underground.

So far as the available analytical data on the waters tested are concerned, there is no apparent general relation between the chemical quality of a water and its radioactivity. This is not surprising, since the emanation content appears to be due, not to dissolved radium, but to contact with radioactive materials, sometimes within a very restricted area.

There was no sharply defined rainy season[3] during 1916 in the places visited. With the exception of the determinations made in April and December, the tests for radioactivity were conducted during months of considerable rain.

Though no systematic study of the relation between the radioactivity and the variation of flowing wells and springs has been made,[4] it may be of interest to point out that Sibul

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[1] N. Sahlbom: Arkiv. Kemi, Min. Geol., 6, No. 3, 1–52 (1915); through Chem. Abstracts, 10, 1134 (1916).

[2] By Mr. B. E. Lednicky, Chief, Division of Mines, Bureau of Science.

[3] For the distribution of rainfall in the Philippines according to locality and season, see A. J. Cox: Philippine Jour. Sci., 6A, 287–296 (1911).

[4] The flow of many springs and deep wells in the Philippines changes greatly in quantity with the tide, though there is no appreciable variation in chemical quality See note on the tidal variation of springs and deep wells in the Philippine Islands. W. G. Heise: Philippine Jour. Sci., 11A, 125–127 (1916).

Springs (Nos. 3 and 4) were tested on two different occasions (as indicated in Table I), once in the middle of the dry season, that is, after two or three practically rainless months, and once during a period of frequent rains. The results of the two determinations, which are practically identical, indicate that deep-seated springs, such as Sibul Springs, may show surprisingly small seasonal variations in radioactivity. It should be pointed out that Sibul Springs show a comparatively slight variation in flow throughout the year, so that the inference from the two isolated determinations just discussed is not considered to be at variance with the findings of others. Thus Ramsey[1] found a greater emanation content in certain springs during period of wet weather and great flow, and Steichen[2] observed an increase in activity in certain Bombay hot springs during the dry season, while the flow of water was considerably reduced. As pointed out by the latter investigator, local conditions may well account for the differences noted.

For the sake of completeness, we have noted in our data all sources of water supply which are popularly considered to have special medicinal virtues. Obviously, either popular opinion is a poor guide to the medicinal value of a water, or else the medicinal properties of water are not to any great extent due to radium emanation content. The waters with perhaps the greatest reputation, namely, Los Baños and Sibul Springs (Nos. 7 and 3), have relatively high radium emanation contents, yet many others regarded as highly, such as Marilao, Pansol (Nos. 5 and 6), Santo Tomas (No. 19), and Klondike (No. 26), contain little or no emanation. Moreover, many waters high on the list, such as Batangas (No. 1), Kiangan (No. 25), Pagsanjan (No. 11), and in general the spring waters near Mt. Banajao (Nos. 8–16), are regarded with entire indifference.

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[1] R. R. Ramsey: "The Variation of the Emanation Content of Certain Springs," Phil. Mag., **30**, 815–818 (1915).

[2] A. Steichen: "The Variation of the Radioactivity of the Hot Springs at Tuwa," Phil. Mag., **31**, 401–3 (1916).

Summary

The radioactivity of about ninety different Philippine waters, chiefly from springs and flowing wells, has been studied. The highest radium emanation content encountered in a deep-well water was equivalent to 2100×10^{-12} grams of radium (per liter); the highest in a spring water was equivalent to 1300×10^{-12} grams of radium.

A test for the actual radium content of about twenty typical sources showed that the radioactivity encountered was due to emanation absorbed from materials with which the ground water had been in contact and was not due to dissolved radium salts. One sample of water showed a scarcely detectible trace of activity due to radium salts in solution; all the others tested gave negative results.

This paper describes a part of an extensive study of Philippine waters, full details of which will be found in the Philippine Journal of Science.

Bureau of Science
Manila, P. I.
February, 1917

ON THE LIGHT ABSORPTION OF AN AQUEOUS SOLUTION OF SODIUM SULPHATE

BY E. O. HULBERT AND J. F. HUTCHINSON

It is well known that the temperature coefficient of the solubility of sodium sulphate in water experiences a marked change at the temperature 32.384° C.[1] If the sudden break in the solubility curve is interpreted to indicate a change in the state of aggregation of the molecules of the salt and of the solvent, one might expect to find also at this temperature changes occurring in the light absorption bands of the solvent and of the solution. The region of the spectrum under examination was from 901 $\mu\mu$ to 1133 $\mu\mu$. The aqueous solution of sodium sulphate was practically as transparent as pure water for this region; therefore, the change was looked for in the water-band which has a maximum of absorption at about 1 μ. It may be stated in advance that no change was found. The experiment was suggested by Dr. A. H. Pfund, of the Department of Physics of the Johns Hopkins University.

The apparatus described in a previous paper[2] was employed. For the purposes of this experiment the cells were surrounded by an electric heating device. The light absorption coefficient α (in the notation of the paper just referred to) was measured for a one molar aqueous solution of sodium sulphate at temperatures 19.07°, 30.0°, 35.5°, 40.0° and 24.1° C, throughout the region of the spectrum from 901 $\mu\mu$ to 1133 $\mu\mu$. Table I shows the experiment data. Columns 2 to 5, inclusive, give the values of α at each wave-length, as the temperature of the solution increased in successive steps; Column 6 gives the values of α taken after the solution had cooled down. The data show that at all the temperatures α remained constant within the error of experiment.

[1] H. C. Dickinson and E. F. Mueller: Bull. Bur. Standards, 3, 640 (1907).
[2] The Journal of Physical Chemistry, 21, 150 (1917).

TABLE I

Wave-length	α				
	19.7° C	30.0°	35.5°	40.0°	24.1°
901 μμ	0.0034	0.0032	0.0036	0.0034	0.0034
920	0.0043	0.0045	0.0045	0.0047	0.0043
940	0.0082	0.0080	0.0084	0.0085	0.0086
960	0.0192	0.0194	0.0193	0.0195	0.0192
979	0.0208	0.0212	0.0210	0.0211	0.0206
998	0.0178	0.0181	0.0180	0.0179	0.0182
1018	0.0136	0.0134	0.0133	0.0131	0.0135
1037	0.0096	0.0094	0.0092	0.0092	0.0095
1056	0.0070	0.0073	0.0074	0.0072	0.0071
1075	0.0067	0.0067	0.0069	0.0067	0.0068
1095	0.0079	0.0078	0.0078	0.0081	0.0081
1114	0.0102	0.0102	0.0104	0.0107	0.0101
1133	0.0158	0.0165	0.0160	0.0163	0.0160

The fact that no modification in the character of the light absorption occurred when the temperature of the solution was above and below the transition point is in accord with the known facts concerning other physical properties of this solution, for in none of these properties has a sudden change been found.[1]

The Johns Hopkins University
June, 1916

[1] Whetham: "Theory of Solutions," p. 79.

A RE-DETERMINATION OF THE HEAT OF VAPORIZA-
TION OF WATER

BY J. HOWARD MATHEWS

A number of years ago an improved method for the determination of heats of vaporization of liquids: was developed by T. W. Richards and the writer.[1] For testing the method, water was chosen as the substance to be vaporized for three principal reasons: it is a substance easily purified, it has a high heat of vaporization, and it is the substance upon which more methods have been tried than any other; consequently it offered us the best possible means of comparison of our method with the methods used by others.

In the development of the method we finally perfected, after trying a considerable number of devices designed to prevent previously recognized possibilities for error, we discovered some exceedingly important sources of error which had been quite overlooked by other workers. For a detailed description of the apparatus and method, and a complete discussion of the sources of error to be avoided or minimized, the original article must be consulted. Briefly, the method was based on one previously suggested by Kahlenberg,[2] in which the liquid was vaporized by means of an electrically heated resistance in a specially designed vessel which could be brought close to the condensing coil which was immersed in the calorimeter. In our modification of this apparatus, the water to be vaporized was contained in a vacuum-jacketed cylindrical vessel constructed as shown in Fig. 1. This vaporizing vessel was connected directly to a block-tin condenser immersed in the water of the calorimeter proper, the various parts of which are shown in Fig. 2.

In the calculation of the heat of vaporization of the liquid condensed in the coil, the assumption has always been made

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[1] Jour. Am. Chem. Soc., **33,** 863 (1911); Proc. Am. Acad. Sci., **46,** 511 (1911).

[2] Jour. Phys. Chem., **5,** 215 (1895).

that all of the vapor was at the boiling point of the liquid at the moment that it condensed in the coil. With the various designs of apparatus heretofore used, with the possible ex-

this assumption is erroneous, for long before the boiling point of the liquid is reached the liquid is giving off vapor which passes into the calorimeter and condenses, and since the heat of vaporization is highly dependent on the temperature of the condensing vapor, the error so introduced into the calculation must have been considerable. Furthermore, in the calculation it has been assumed heretofore that all of the condensed liquid cools from a definite temperature, *viz.*, the boiling point, to the temperature of the calorimeter. This assumption also is not true for the methods previously used, with the exception of that of Luguinin. In our method both of these serious errors are avoided, for the vapor does not begin to pass down the delivery tube to the condensing coil until the liquid has been boiling for some time—the time during

Fig. 1

which temperature readings are taken to ascertain exactly the correction to be applied for radiation and conduction of heat from the vaporizer to the calorimeter water.

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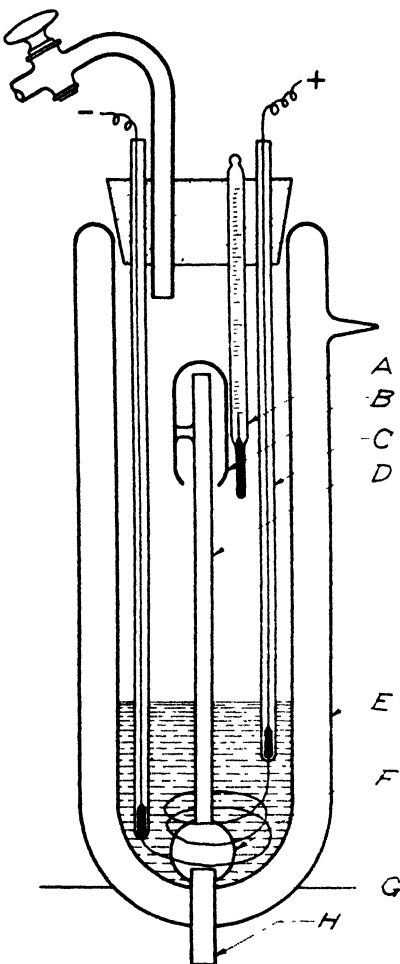
[1] Ann. Chim. Phys., (7) **7, 251** (1896).

J. Howard Mathews

Early in our work it was observed that the values ob-
tained for heats of vaporization depended on the rate at which
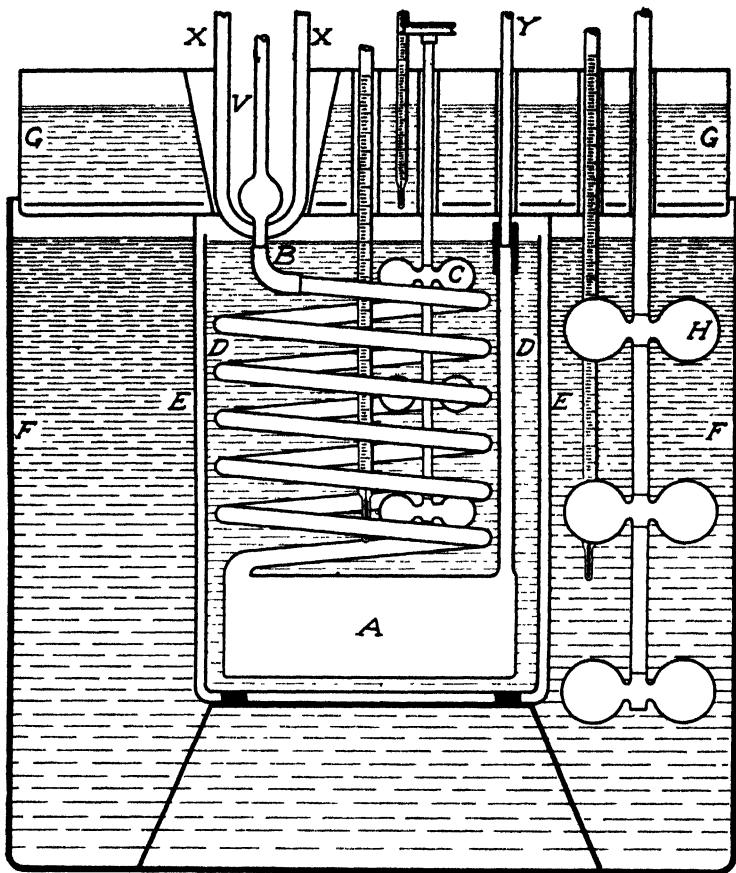
Fig. 2

The calorimeter. The vaporizer (V) is set within a large hole (XX) in
the cover. At B is attached the condenser A immersed in water con-
tained in the calorimeter. Between the jacketing vessels E and F is
dilute alkali, into which sulphuric acid is dropped in order that the
temperature of the surroundings should keep pace with that of the
calorimeter proper. C is a stirrer within the calorimeter, H one in the
outside vessel

vapor passed into the condensing coil. We succeeded in
showing that this effect is due to premature condensation of

the vapor, *i. e.*, condensation of the vapor at some point where the heat given out in the act of condensation would not be transmitted to the calorimeter while the water produced by this condensation would be delivered to the coil. By the introduction of a trap at the bottom of the chamber in which the liquid is vaporized (see F, Fig. 1) and by making the distance from this trap to the calorimeter water as short as possible (a few mm only) the effect produced by this premature condensation was reduced to a minimum. The trap also served to catch and retain any liquid which may have gotten into the delivery tube by spattering. A drop or two of liquid was always found in this trap after the experiment; hence the trap was always emptied between determinations.

While the trap and the shortening of the distance between vaporizer and calorimeter water naturally minimized the effect due to premature condensation, the effect was not wholly eliminated, since it is impossible wholly to eliminate the zone in which premature condensation may take place. To get the true heat of vaporization, however, it is only necessary to conduct several experiments in which the rate of condensation of vapor is made to vary considerably, then plot the times necessary for the condensation of one gram against the values obtained for the heats of vaporization, and by a slight extrapolation of the linear curve so obtained the true heat of vaporization is found, that is, the heat of vaporization which would have been obtained had the vapor passed into the calorimeter under conditions such that no premature condensation could occur.

Curiously, no previous workers have ever made mention of the dependence of the experimental values on the rate of condensation. With the most perfect apparatus we were able to devise, this effect was so marked that serious error would have been made had it not been recognized and corrected for, and with the less perfect methods used by former workers, where the possibility of error was not even recognized, the error must have been very serious indeed since generally the design of apparatus was such as to necessitate considerable premature condensation.

Preliminary work on the heats of vaporization of a number of substances other than water showed the same effect, in degree depending on the difference in temperature between the temperature of the calorimeter and the boiling point of the liquid. Where this difference was great the loss of heat by premature condensation was naturally great; and where the difference was small the effect was small.

Previous to our work it had been noted that the values for the heats of vaporization of liquids as determined by the condensation method were usually lower than the values obtained by the electrical method, where the energy required to vaporize a gram of the material is measured. In this connection it is interesting to find that the values found by our method agree remarkably well with the values obtained by the most refined of the electrical methods, not only for water but for other substances as well. As the average of two closely agreeing series of determinations of the heat of vaporization of a true gram of water at $100°$, made with two different vaporizers, the value 538.9 cal$_{21°}$ was found. This value agrees well with the value obtained by Henning,[1] who found the value 539.5 cal$_{21°}$, using a refined electrical method. Work now well under way on the heats of vaporization of a large number of compounds confirms the belief that the values which have been obtained by the electrical methods are not considerably too high, as had formerly been supposed, but rather that the values which have been obtained by the condensation methods are the ones which are at fault.

Soon after the appearance of our paper in 1911, A. W. Smith[2] published an account of his determinations of the heat of vaporization of water. Proceeding on the assumption that all former condensation methods had necessarily given low results due to "priming," *i. e.*, the carrying over of unvaporized liquid along with the steam, Smith developed a method in which the vaporization took place from a relatively quiet surface. The vaporization was brought about by pass-

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[1] Drude's Ann., **21**, 849 (1906).

[2] Phys. Rev., **33**, 173 (1911).

ing dry, pre-heated air through the vaporization chamber, the water vapor being subsequently removed from the air by condensing most of it and absorbing the remainder in sulfuric acid. The energy necessary to just overcome the cooling effect of this evaporation, *i. e.*, to maintain the liquid at a constant temperature (98.7°), was supplied electrically, and could be determined by a potentiometric method. By changing the rate of evaporation it was possible to eliminate the necessity of a knowledge of the water equivalent of the apparatus and the amount of heat conducted out through the heating wires, as well as a knowledge of the amount of heat received by the water in the vaporization chamber from the surrounding steam jacket. Since but one temperature was read a complete standardization of the thermometer was unnecessary.

Twenty determinations were made at 98.07°, and the results calculated to 100°. The average of all of these determinations, in which the extreme variation was 2.44 calories, was 540.7 mean calories, or the same number of 15° calories since these are of equal magnitude. The difference between this value and the value which has generally been accepted heretofore was ascribed wholly to priming.

Some fifteen years previous to the work of Smith, Harker[1] had developed a method designed to eliminate danger of error through priming. In this method the vapor was conducted through a pre-heater to insure the removal of all liquid particles before it entered the condensing coil in the calorimeter, the amount of pre-heating being determined by means of a thermo-couple so placed that it gave the temperature of the vapor entering the condensing coil. Correction was made for the excess heat introduced by this pre-heating. Harker concluded from his experiments that the true heat of vaporization of water at 100° is 540 calories. However he considered his experiments to be only preliminary ones, and gave no data. His method has certain features which appear to be somewhat faulty, and likely to give somewhat too high results. These

Mem. Manchester Lit. and Phil. Soc., 10, 38 (1896).

were discussed by Richards and the writer in 1911.[1] The particular virtue of Harker's method lies in the way in which premature condensation was avoided, rather than in the elimination of priming. It is regrettable that further experimentation was not carried out.

Since the question of the possibility of error through priming is so important in measurements of heats of vaporization, it was imperative that the question be subjected to experimental test. Accordingly, the following methods of attack were used:

In the first the heat of vaporization apparatus as used by us at Harvard was set up as for a determination. In the vaporizer was placed a 1 percent solution of potassium permanganate instead of pure water. Now if priming, *i. e.*, the purely mechanical disengagement of liquid particles from the boiling solution, took place, and if these particles were not subsequently removed before condensation took place in the coil it is evident that permanganate should be found in the condensed liquid. Two tests were made, with different rates of vaporization, both of which exceeded the rate used in the measurements of heats of vaporization. In the first 9.3 grams were condensed in three minutes; in the second 15 grams were condensed in three minutes, and in neither case was the slightest trace of permanganate detectable in the distillate. A capillary tube was inserted in the delivery tube of the vaporizer, from beneath, and the trap was washed out with a jet of water. No permanganate was found in the trap. Since these vaporizations were made at a much greater rate (one of them 100 percent greater) than any of the vaporizations in the actual measurements of heats of vaporization, it seems certain that no particles of unvaporized water were carried over mechanically from the boiling liquid in the vaporizer.

The second method of attack was quite different, but perhaps equally as conclusive. In this the vapor above water boiling vigorously in a distilling flask was examined for the

presence or absence of particles by observing whether it would show the Tyndall effect. The flask used was one having a wide neck, about 3 cm in diameter. Through this a powerful, condensed beam of light was projected from an arc; the room itself was dark. When the beam of light was brought down to within 5 cm of the boiling water a number of points of light could be seen in the path of the beam, but when it was raised to 10 cm no points of light were observed, even with very vigorous boiling. The water was boiled both by means of the electric current passing through a submerged resistance coil, and by means of a burner placed beneath the flask. In neither case was any semblance of a cone visible.

It therefore seems safe to conclude that in the vaporization which takes place under the conditions of experiment in the measurements made by the method of Richards and the writer no anxiety need be felt regarding the possibility of error through priming. The vapor rising from the boiling liquid has to pass through a hood placed over the upper end of the delivery tube, thence down through this narrow tube to a trap at the bottom of the vaporizer. It is well known to bacteriologists that an effective means of freeing air of bacteria is to pass it through a narrow tube, the inside walls of which are wet. It is also equally well known to those who have occasion to use the ultra-microscope that the most convenient and effective way to get air which is optically empty, *i. e.*, to free it entirely of all suspended matter, is to pass air through such a tube. The chance that particles of liquid torn from the boiling water might traverse all of the pitfalls provided for them in this apparatus and eventually pass into the condensing coil seems very slight indeed; and the first line of experimentation (with the permanganate solution) shows conclusively that unvaporized particles are not so carried over. Doubtless priming does occur under certain circumstances, such as violent boiling under pressure as in steam boilers, but that there is possibility of any uncertainty in the values of heats of vaporization as determined by this particular method seems quite out of the question.

Since the Harvard work was completed the writer has had occasion to build up an entirely new set of apparatus for the measurement of heats of vaporization. In principle the apparatus as it now stands perfected is the same as that used in the former research, the difference being in details of construction.

The two-compartment adiabatic calorimeter formerly used has been replaced by one of the "submarine type,"[1] in which the calorimeter proper is surrounded by one and the same bath of alkali. The stirrer in the alkali bath, of the propellor type, has ten blades and is driven at a high speed by an electric motor. The temperature control in the new form of adiabatic calorimeter is much more satisfactory than in the one formerly used. It is possible to keep the temperature of the outer bath within a few hundredths of a degree of the temperature of the calorimeter proper during the whole determination. The stirring of the liquid in the calorimeter proper is accomplished by means of a stirrer consisting of three flat, perforated brass rings attached to two slender brass rods which pass through tubes soldered into the cover and are fastened to a cross bar of hard rubber which in turn is attached to a stout brass rod which is actuated by an electric motor operating through an eccentric. Both rings and rods are thinly plated with nickel. This stirrer is made to thrust up and down at a lively rate—about 100 strokes per minute—and stirs the water very effectively The calorimeter proper (of about 1400 cc capacity) is of thin sheet copper, lightly nickel plated inside and out and highly polished to reduce radiation. The condensing coil is of platinum, and has a capacity of about 80 cc. This coil hangs suspended within the stirrer.

To determine the rise in temperature a Beckmann thermometer having a large, long mercury bulb is used. This particular thermometer was selected from a group of a dozen. The scale divisions were fine and sharp, enabling accurate readings to be made. It was standardized by careful com-

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[1] See Richards and Jesse: Jour. Am. Chem. Soc., **32,** 268 (1910).

parison with: (1) a Beckmann thermometer which had been standardized by the Physikalisch-Technische Reichsanstalt, corrections for which were given to 0.001°; (2) an enclosed scale "Normal" thermometer made by Goetze, graduated to 0.01° between 18 and 25°, corrections for which (in thousandths of a degree) had been furnished by the United States Bureau of Standards; (3) a second "Normal" thermometer of similar type, graduated to 0.01° between 14 and 24°, corrections for which (in thousandths of a degree) had been furnished by the Bureau of Standards; and (4) a Leeds and Northrup resistance thermometer and bridge which also had been standardized by the Bureau of Standards. Temperatures could be estimated to 0.0005° by means of this thermometer and bridge.

Comparisons of all of these thermometers were made at the same time, under *adiabatic conditions.* One observer read the mercury thermometers while a second manipulated the bridge. All the thermometers were read at least twice for each point at which comparisons were made, these points being at intervals of about 0.1° throughout the Beckmann scale. The comparisons showed the mercury thermometers and resistance thermometer standardized by the Bureau of Standards to be consistent among themselves, within the limit of error of reading, while the readings taken from the thermometer standardized by the Reichsanstalt did not agree so well with the thermometers standardized by the Bureau. For this reason more reliance was placed on the thermometers standardized by the Bureau in calculating the corrections to be applied to the thermometer used in this research. The thermometers were compared in a room whose temperature was regulated to 20°–21°, since the thermometer being standardized was to be used in a room maintained at this temperature.

The greatest single improvement in the apparatus over that previously used consists in the substitution of a vaporizer made of thin, transparent quartz for the vaporizers made of glass. Considerable difficulty was experienced in even getting the glass vaporizers made, to say nothing of the danger

of breakage under the severe strains they were subjected to in service. Although the initial cost of such a complicated piece of quartz apparatus is considerable it is in the long run more economical than glass on account of the decreased breakage.[1] The position of the quartz vaporizer was carefully adjusted so that the level of the water in the calorimeter came up about one centimeter higher than the point where the delivery tube joins the outer wall of the jacket. This depth of immersion is necessary because a great deal of heat is undoubtedly liberated in the portion of the quartz tube which dips into the water of the calorimeter. The vaporizer was always maintained in exactly this same position, so that the water equivalent of the system should remain constant. If in different determinations different amounts of surface of the quartz were wetted the water equivalent naturally would vary.

Water Equivalent

The accurate determination of the water equivalent of the calorimetric system heated by the condensing vapor presented some difficulties. The equivalent of the calorimeter proper, stirrer, condensing coil and thermometer can be calculated with sufficient accuracy (assuming that the specific heats are sufficiently well known), but the determination of the equivalent of the part of the quartz vaporizer immersed in the water cannot be calculated directly. The problem was solved in the following manner: First, the total water equivalent of the entire calorimetric system was determined by an electrical method, then the quartz vaporizer was removed and the total water equivalent again determined. The difference between these two values must represent the water equivalent of the quartz, and this value can be added to the value calculated for the rest of the calorimetric parts. It is of course necessary that the quartz be immersed *always to the same depth*, else the water equivalent of the sys-

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[1] The quartz apparatus used in this work was made by The Hanovia Chemical and Manufacturing Co., of Newark, N. J.

tem will vary. This condition was met by fixing the vapor-izer in the cover of the calorimeter so that it was always in the same position; then to secure the same depth of immersion it is only necessary that the same volume of water be placed in the calorimeter each time.

The apparatus was set up exactly as used in the measurement of heats of vaporization, with the following exception: On account of lack of room in the calorimeter for both, the platinum condensing coil was removed and in its place was substituted an electrical heating element consisting of a suitable length of fine nichrome wire to give a resistance of about 32 ohms, contained in a thin, flat metallic sheath. The wire was wound on a mica frame and was enclosed in a flat brass case 5 cm long, 4 cm wide and 3 mm thick, to which was soldered a light brass tube 13.5 cm long and 4 mm in diameter. One end of the nichrome wire was soldered to the bottom part of the case, the other being soldered to a stout rubber-insulated copper wire which passed out the tube. The wire on the mica frame was insulated from the containing case by thin mica sheets, one on each side of the frame. The resistance element so prepared was given a light coating of copper, on which was then deposited a thin layer of silver. In calculating the water equivalent of this element the assumption was made that it was composed entirely of brass, since the weights of nichrome, mica, copper and silver are, when taken together, not more than two grams.

The heating element was placed in such a position that the sheath containing the resistance wire was about at the center of the calorimeter. The tube of the element passed through dry corks fitting tightly into a brass tube soldered into the cover of the calorimeter. The current was brought to the heating element by heavy (No. 10) insulated copper wire. Connection was made through freshly brightened brass connectors, with set screws, to secure perfect electrical contact. Two No. 10 insulated copper wires were soldered to the leads carrying the current, the junction of the wires being about one centimeter back of the connectors. These wires led to a

heavy double-pole, double-throw switch, by means of which either a voltmeter or potentiometer could be bridged across the circuit at will, to ascertain the potential drop across the terminals of the heating element.

With the heating element so placed, the amount of water necessary to bring the level to the desired point on the quartz vaporizer was carefully determined, and this exact amount of water was used in all of the determinations.

The calculation of the water equivalent of the apparatus by the electrical method can best be described by means of a sample calculation. The symbols used have the following significance:

H = the water equivalent of the calorimetric parts,

Q = the quantity of heat (in 20° calories) liberated by the passage of the current through the element,

W = the weight (reduced to *vacuo*) of the water in the calorimeter,

R = the rise in temperature of the calorimetric system,

E = the potential drop across the terminals of the heating element,

F = the value of the faraday in coulombs (96490),[1]

w′ = the weight of silver deposited in the coulometer.

The data for the following calculation were obtained with the quartz vaporizer in place:

Data:

Weight of water in calorimeter (W)	1376.5 grams
Rise in temperature of the system (R)	4.820°
Voltage drop across terminals of heating element (E)	35.000 volts
Weight of silver deposited in coulometer (w′)	0.9162 gram
Mean temperature of calorimeter	19.4°
Value of the calorie at this temperature	4.180 joules

Calculation:

$$H = \frac{Q - (W \times R)}{R}$$

But,

$$Q = \frac{(F \times w' \times E)}{(107.88 \times 4.180)} = \frac{(96490 \times 0.9162 \times 35.000)}{(107.88 \times 4.180)}$$

[1] Value found by the Bureau of Standards, using the silver coulometer.

Then,

$$H = \frac{\left(\dfrac{96490 \times 0.9162 \times 35.000}{107.88 \times 4.180}\right) - (1376.5 \times 4.820)}{4.820}$$

$H = 47.0$ grams.

It will be observed that the quantities which have to be determined are: (a) the weight of water in the calorimeter, (b) the rise in temperature of the system, (c) the voltage drop across the terminals of the heating element, and (d) the weight of silver deposited in the calorimeter.

The water used was freshly distilled from alkaline permanganate. A definite quantity was placed in the calorimeter, the weight being constant to 0.05 gram. The weighing was done on a large Bunge balance capable of carrying a load of 2 kilos with a sensitiveness of one-tenth milligram. This filling of the calorimeter was left for the last operation before putting on the cover, in order to minimize evaporation. The amount of water evaporating from the calorimeter during a determination was negligible, as the volume of air in the compartment occupied by the calorimetric system was very small; and the brass tubes through which were inserted the thermometer, heating element and quartz vaporizer were entirely closed, to prevent circulation of air through them. For the same reason the brass rods of the stirrer passed through closely fitting cork sleeves. The weights of water used in the calorimeter were therefore certain to one or two parts in fourteen thousand.

The temperature rise was determined with the carefully standardized thermometer, already described. The temperature of the room was automatically controlled by a thermostatic device, and was kept at the temperature at which the thermometer had been standardized; hence no correction for exposed mercury thread was necessary. The temperature of the system was read at intervals of one minute for some time before the current was turned on to the heating element, and was read similarly for some time after the current had been turned off. A small electric buzzer attached

to the top of the thermometer eliminated the sticking of the
mercury thread. The temperature readings were made
with the aid of a reading telescope mounted on the thermo-
meter. The scale was illuminated from behind; the readings
to $0.001°$ could be made with certainty. The maximum
temperature (which of course remained constant, as condi-
tions were adiabatic) was attained within one minute after
the current ceased passing through the heating element.
The temperature rise, usually about $4.8°$, took place at the
rate of about $0.4°$ per minute, and of course took place regu-
larly. As the zero of the Beckmann thermometer in the
bath of alkali had been set identical with the zero of the Beck-
mann in the calorimeter (to $0.01°$), it was easy to admit
sulphuric acid into the violently agitated alkali at such a
rate that the temperatures of the calorimeter and its environ-
ment did not differ by more than $0.05°$ at any time and were
usually within 0.01 or $0.02°$. One observer (my assistant,
Mr. R. V. Williamson, to whom I am greatly indebted) de-
voted his entire attention to the adiabatic control of the
calorimeter throughout the whole experiment. The readings
of temperature rise are probably as certain as temperatures
can be read with the mercury thermometer, *i. e.*, to within
$\pm 0.001°$. The temperature rise was therefore certain to
about one or possibly two parts in five thousand.

The current for the heating element was taken from a
group of storage batteries, isolated from the remaining bat-
teries in the battery room. The potential drop required to
give the desired rate of temperature rise was 35 volts. In a
number of preliminary experiments made to test the method
and to become familiar with the exacting technique required,
a large Weston Laboratory Standard voltmeter with 12-
inch scale was used to ascertain the voltage. This voltmeter
was standardized by means of a Brooks potentiometer and a
standard Weston cell, certification of which had been made
by the Bureau of Standards.[1] By means of a five-inch lens

mounted above the scale, readings to 0.02 volt could be estimated. By means of a suitable sliding resistance, the potential
drop could be kept constantly at 35 volts to within ±0.02
volt. As a part of the current passed through the voltmeter
a correction had to be made for the amount of energy so lost.
This was determined by putting the voltmeter in series with
a silver coulometer, with the voltmeter registering 35 volts,
and determining the amount of silver deposited at the end
of several hours. The correction so found amounted to
about 0.14 percent of the total current used, and agreed
closely with the correction as calculated from the known
resistance of the voltmeter (about 31,000 ohms) and that
of the heating element (about 32 ohms).

It was feared, however, that the voltmeter readings
might not be sufficiently accurate and certain, and in the
final work here reported a Leeds and Northrup Type K
potentiometer and Weston standard cell were substituted
for it. A volt box with a ratio of 1 to 100 was used to reduce
the potential drop to a value which could be measured accurately. The volt box was improvised from a large Wolff
resistance box, having a total resistance of approximately
100,000 ohms, the individual resistances of which as well
as the total were standardized by means of a large Leeds
and Northrup Wheatstone bridge having 10 ratio coils. In
this standardization a Leeds and Northrup Type HN wall
galvanometer was used as indicating instrument. The total
resistance of the box was found to be 99,937 ohms, while the
sum of the individual resistances, as measured separately,
was 99,934 ohms. The resistance value for the particular
1000 ohm cell used to pick off potential drop for the potentiometer was checked and re-checked using different combinations of the ratio coils, all of which gave closely agreeing
values. The mean of these values showed this coil to have
a resistance of 999.83 ohms. The volt box therefore had a
ratio of $\frac{999.83}{99934}$. To secure a potential drop of exactly 35
volts required that the potentiometer be set to read
$\frac{999.83}{99934} \times 35 = 0.35017$ volt.

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The indicating instrument used with the potentiometer was a Siemens and Halske galvanometer having a very short period and giving a deflection of 1 mm on a scale 1 meter distant for a potential of 12×10^{-7} volts. The sensitiveness was somewhat further increased by increasing the distance to 120 cm.

The sliding contact rheostat already mentioned was supplemented by placing in series with it a coarse slide wire of manganin, whose traveling contact was operated by a micrometer adjustment. The sensitiveness of the galvanometer was such that a movement of 2 mm for the slider produced a noticeable deflection on the scale. It was found possible to maintain the voltage constant to ± 0.001 volt.

The Weston standard cell used with the potentiometer was one which was kindly loaned by the Wisconsin Standards Laboratory. It had been standardized a few months previously by the Bureau of Standards, and was compared at the time of use with a similar Weston cell which had been standardized by the Bureau more recently. This comparison was made by means of an excellent Wolff potentiometer in the Wisconsin Standards Laboratory. The value agreed well with that previously found by the Bureau. The potential of this cell was 1.01872 at 21.5°.

The coulometer used was of the Richards porous cup type, platinum dishes of about 275 cc capacity being used as cathodes, and electrolytic silver as the anode. The unglazed porcelain cup was cleaned by digestion with hot nitric acid for several hours, after which the acid was completely removed by repeatedly washing and soaking in pure water until the water showed no acid reaction. While not in use the cup was kept immersed in silver nitrate solution. The electrolyte was made from Merck's pure silver nitrate, which was found to be neutral. A 10 percent solution was used, fresh portions being used for each determination. The precautions recommended by the Bureau of Standards[1] were observed in handling and drying the silver deposit. The de-

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[1] Bull. Bureau of Standards, **13,** 479 (1916).

posits were weighed on a Spoerhase-Staudinger balance, sensitive to $^1/_{50}$th milligram, the weighings being made with a set of platinum plated Sartorius weights which had been standardized by the Bureau of Standards. As the deposits weighed about 0.9 gram, it is felt that the amounts of current used were determined to one part in nine thousand.

Having assembled the various parts of the apparatus, the approximate resistance to maintain a potential drop of 35 volts across the terminals of the heating element was determined by putting in a coulometer similar to the one to be used in the determination and adjusting the rheostat to the position required to give a reading of 35 volts on the voltmeter. This coulometer was then removed and the one to be used was put in its place; and the potentiometer was bridged in, in place of the voltmeter, by means of the double throw switch. Meantime the adiabatic bath was being adjusted to the proper temperature and readings of the temperature of the calorimetric system were made at intervals of one minute. When all was in readiness, the initial temperature thus having been determined exactly, the current was turned on and the necessary slight adjustment was quickly made on the rheostat (or extended wire) to bring the voltage precisely to 35 volts. One observer watched the galvanometer and kept the voltage constant by keeping the galvanometer indication at zero by means of the slide wire, while the other gave his entire attention to the exact control of the adiabatic bath. When the desired rise in temperature, about 4.8°, had been attained, the current was cut off and temperature readings were again taken for some time at intervals of one minute. The initial and final temperatures were read on stationary mercury threads, the temperature of the calorimeter remaining constant during the two periods. The coulometer was dismantled immediately the current was cut off and the deposit of silver was washed and dried, the washings being examined for particles of disengaged silver. In none of the runs here reported were weighable amounts of silver found in the wash-water.

The data and results for the six determinations made to ascertain the water equivalent of the calorimeter and parts, with the quartz vaporizer in place, appear in the following table:

TABLE I

Weight of water in colorimeter (*vacuo*) Gms	Rise in temperature °	Mean temperature of calorimeter °	Voltage drop across heating element	Weight of silver deposited Gm	Total water equivalent Gms	Water equivalent of all calorimetric parts Gms
1376.5	4.810	20.3	35.000	0.9137	1422.6	46.1
1376.5	4.769	20.3	35.000	0.9065	1423.5	47.0
1376.5	4.820	20.2	35.000	0.9162	1423.5	47.0
1376.5	4.812	20.2	35.000	0.9147	1423.6	47.1
1376.5	4.793	20.2	35.000	0.9103	1422.5	46.0
1376.5	4.868	20.2	35.000	0.9254	1423.7	47.2

Mean value = 1423.2 gms   46.7 gms

Since the heating element was substituted for the platinum condensing coil (there not being room for both) a calculation had to be made to determine what change in water equivalent was caused by this substitution. The weight of the heating element was 52.5 grams. Considering this as being composed entirely of brass, its water equivalent was 52.5 × 0.091 = 4.78 grams. Since the water equivalent of the condensing coil was 150.3 × 0.032 = 4.81 grams, the difference in water equivalent caused by the substitution of the heating element for the platinum coil is negligible. Hence the water equivalent of the calorimetric parts of the apparatus as assembled for measurements of heats of vaporization would appear to be 46.7 grams.

The quartz vaporizer was then removed and four determinations of the water equivalent of the system remaining were made in precisely the same manner. The data and results calculated therefrom appear in the following table.

From the results shown in these two tables it is evident that the amount to be added for the water equivalent of the quartz is 1423.2 — 1419.0 = 4.2 grams.

TABLE II

Weight of water in calorimeter (*vacuo*) Gms	Rise in temperature °	Mean temperature of colorimetric °	Voltage drop across heating element	Weight of silver deposited Gm	Total water equivalent Gms	Water equivalent of all calorimetric parts Gms
1376.5	4.836	20.3	35.000	0 9162	1418.8	42.3
1376.5	4.293	19.9	35.000	0.8134	1419.0	42.5
1376.5	4.839	20.2	35.000	0.9166	1418.6	42.1
1376.5	4.830	20.2	35.000	0.9155	1419 5	43.0

Mean value = 1419.0 gms   42.5 gms

The water equivalent of the entire apparatus composing the calorimetric system may now be calculated.

The copper calorimeter was made with tightly crimped joints to minimize the amount of solder required to make it tight. The amount of nickel used in plating was small, and since its specific heat is nearly that of copper the entire calorimeter can be considered as being composed of copper. As its weight was 275.2 grams and the specific heat of copper at 20° is 0.093, the water equivalent of the calorimeter was 25.59 grams. The stirrer was made of brass and was lightly plated with nickel. Since but a small length of the brass rods projected above the calorimeter, where they were fastened to the hard-rubber cross piece, the entire weight of the stirrer was taken in calculating its water equivalent. Its weight was 90.9 grams. Taking the specific heat of brass to be 0.091 at 20° the water equivalent for the stirrer would be 8.27 grams. The condensing coil was made of platinum and, as mentioned above, its water equivalent was 150.3 × 0.032 = 4.81 grams. The water equivalent of that portion of the Beckmann thermometer which was immersed in the calorimeter water (the depth of immersion of course always being the same) was determined by the method of Ostwald,[1] and was found to be 1.74 grams. The sum of all of these quantities, including the value found for the quartz, was 44.6 grams.

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[1] Ostwald-Luther: "Physico-chemische Messungen," p. 300 (1910)

It will be noted that the value obtained by the electrical method for the water equivalent of the various parts is about two grams higher than the value obained by calculation from the known weights and specific heats of the parts. It must be remembered, however, that this difference is really a difference of two grams in fourteen hundred and twenty rather than two giams in forty-four, since by the electrical method the water equivalent of the parts is gotten by difference, *i. e.*, the total water equivalent minus the water equivalent of the water placed in the calorimeter. Because of a difficulty which is inherent in the electrical method, and for which no really satisfactory correction can be made, *viz.*, the error which may arise from the possible flow of heat out of the calorimeter along the stout copper wires used to carry the electric current for heating, perhaps more reliance should be placed on the value for the water equivalent as determined by calculation from the known weights and specific heats, although the electrical measurements were made with the utmost care. The temperature of the room, during the measurements made by the electrical method, was maintained at a point 0.5 to 1.0° higher than the mean temperature of the calorimeter, to minimize the tendency for heat to flow out of the calorimeter during the heating period. The fact that the initial readings and final readings of the temperature of the calorimeter, surrounded by its adiabatic bath, remained constant showed that no appreciable quantity of heat was flowing out from or into the calorimeter along the copper wires during either of these periods. Moreover the resistance wire in the heating element was inclosed in a very thin, flat sheath which was immersed several centimeters under the level of the well-stirred calorimeter water. The heat must have been given up very quickly to the calorimeter water because of the construction of the element, a conclusion which is further supported by the fact that after the current was shut off the temperature ceased to rise almost immediately. It seems unlikely that either the tube supporting the sheath or the copper wire running through this tube were at a temperature

appreciably higher than the calorimeter water, hence there should have been little, if any, loss of heat by conduction out of the system along the copper wires attached to the heating element. However this possible source of error may be responsible for the small difference in the total water equivalent (a difference of but 0.14%) as determined in the two ways. Of course there remains one other alternative; the specific heats of the substances composing the calorimetric system may not be known with sufficient accuracy. Should it later develop that such is the case a recalculation can be made from the data here reported. In the calculations of the heat of vaporization of water reported in this paper I have used the value calculated from the weights of the various parts and the specific heats which seem to be most reliable. The electrical measurements have been used to ascertain the water equivalent of that part of the quartz vaporizer which is wetted by the calorimeter water when the apparatus is in use.

Since the correctness of the value for the heat of vaporization is dependent on a very exact knowledge of the water equivalent of the apparatus, it seemed desirable to check this value by an additional method. This third method consisted in introducing into the condensing coil of the calorimeter a quantity of hot water, at a known temperature, noting the rise in temperature of the calorimetric system, and ascertaining the quantity of water by weighing the coil after dismantling the apparatus. This method will be referred to in this paper as the "hot water method."

The apparatus used was one designed in collaboration with T. W. Richards in 1908 for the determination of the specific heats of liquids, and has not previously been described. The water is heated, by an electrically heated resistance coil of platinum wire, in a container closely resembling the vaporization flask already described. This vessel (see Fig. 3) is made of transparent quartz, is vacuum jacketed, and the inner walls (*i. e.*, in the vacuum chamber) are silvered to about half the height of the vessel. Passing through the bottom of this flask is a short delivery tube, into the top of which is

ground a long quartz capillary tube, which serves as a tight stopper. The platinum condensing coil is attached to the lower end of this delivery tube, the end of the platinum spiral being flared somewhat so that the delivery tube sets down into it a few millimeters. Connection between the two is made by a very short piece of rubber tubing. The outside dimensions of this quartz vessel are approximately the same as those for the vaporizer. Care was taken to immerse this new vessel to the same depth that the quartz vaporizer is i m m e r s e d in measurements of heats of vaporization.
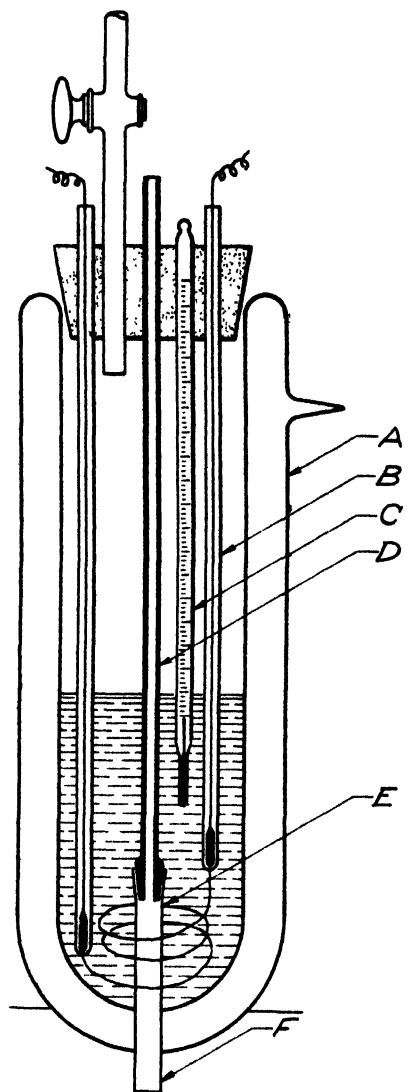
A delivery tube passing out through the stopper and to a condenser allows the escape of steam while the water is being boiled.

A Landsberger thermometer graduated to $0.05°$ and capable of being read to $0.01°$ was inserted through the stopper, with its bulb immersed in the water. The entire mercury thread was within the flask, the reading being made through the walls with the aid of a reading lens.

A suitable quantity of pure, freshly distilled water was placed in the flask and was boiled for some time by the cur-

Fig. 3

rent. Readings of the temperature of the calorimetric system were taken for some time, at intervals of one minute. After the temperature rise per minute had thus been ascertained with certainty, and the exact temperature of the boiling water had been noted, the boiling was discontinued by opening the line switch, the quartz stopper was immediately raised for the few seconds necessary for the desired quantity of water to run into the coil in the calorimeter, the stopper was again inserted and boiling resumed by closing the switch. The platinum heating coil in the boiling chamber was always placed below the top of the delivery tube, so that it was always entirely immersed in water. Immediately the water began to run into the platinum condensing coil in the calorimeter, acid was delivered into the alkali bath at a rate such that the temperature of this bath rose simultaneously with that of the calorimeter. Since the boiling was interrupted for but a few seconds, the temperature of the water remaining in the flask did not change appreciably, and consequently the radiation and conduction of heat to the calorimeter remained regular. Although the delivery of the water took but a few seconds (about fifteen) all of its heat was not given up so quickly. In fact about ten minutes were required for the delivery of all of the heat to the calorimetric system. Temperature readings were taken at intervals of one minute until the successive readings differed by the same amount, showing that the water in the coil had ceased to give out heat to the calorimeter. This amount of change per minute is naturally somewhat less than the change per minute in the fore period, since the difference in temperature between the boiling chamber and the calorimeter system has been diminished by about five degrees, and also because of the fact that the water equivalent of the system in the after period is some sixty or so grams greater than it was in the fore period.

The amount of water entering the coil can be determined exactly by weighing. However, the 18 mm of quartz delivery tube immersed in the calorimeter water has its internal walls wetted by the water flowing through it, and usually one small

drop was found hanging inside this tube when the apparatus was dismantled. Since the heat that was contained in this water left in the delivery tube was transmitted to the calorimeter water it is necessary to know approximately how much was left in the tube. It was estimated that this amounted, on the average, to about 0.1 gram. It certainly was not less than this amount, nor was it probably more than 0.15 gram. In the calculations following, a correction of +0.1 gram has been made to the weights of water actually contained in the platinum coil.

It was necessary to know very exactly the temperature at which the water was delivered to the coil. The thermometer used for this purpose could easily be read to 0.01°, but to get this degree of accuracy it was necessary to determine the thermometer correction after each experiment. Immediately after use each time, the correction to be applied to the reading of the boiling point of water was determined by hanging the thermometer in live steam in a thermometer tester, the whole instrument being in the steam. The temperature of the steam was ascertained by reading the barometer, applying the necessary corrections and consulting the tables. The barometer was of the Weather Bureau type and was standardized by comparison with the United States Weather Bureau Barometer at the Madison station.

The method of calculation can again best be shown by an example.

Data:

Time when reading was taken	Observed thermometric reading (uncorrected)	Increase in temperature per minute
11 : 05	0.307°	
11 : 06	0.329	0.022
11 : 07	0.351	0.022
11 : 08	0.373	0.022
11 : 09	0.396	0.023
11 : 10	0.419	0.023
11 : 11	0.442	0.023
11 : 12	0.464	0.022
11 : 13	0.486	0.022
11 : 14	0.508	0.022
11 : 15	0.530	0.022
11 : 16	0 552	0.022
11 : 17	0.574	0.022
11 : 17 Water run into coil		
Current off 16 seconds		
11 : 21	4.140	
11 : 22	4.198	0.058
11 : 23	4.239	0.041
11 : 24	4.270	0.031
11 : 25	4.296	0.026
11 : 26	4.320	0.024
11 : 27	4.343*	0.023
11 : 28	4.365	0.022
11 : 29	4.386	0 021
11 : 30	4.408	0.022
11 : 31	4.429	0.021
11 : 32	4 450	0.021
11 : 33	4.471	0.021

	As read from Beckmann	Correction to reduce to true temperature	True temperature hydrogen scale
Final temperature	4.343°	17.772°	22.115°
Initial temperature	0.574	17.754	18.328

Rise in temperature 3.787ˈ

* Point at which water in coil ceased to give out heat.

Rise due to radiation and conduction = 10 × 0.0215 =   0.215°
Rise in temperature due solely to heat given out by cool-
   ing of water run into coil   3.572°
Mean temperature of calorimeter   20.2°
Barometric pressure (corrected)   743.8 mm
True temperature of steam in thermometer tester   99.40°
Thermometer reading for steam in tester   99 26°
Correction for thermometer   +0.14°
Thermometer reading for boiling water   99.58°
True temperature of boiling water   99.72°
Heat given out by cooling of one gram of water from the
   boiling temperature to the mean temperature of
   calorimeter = (99.72 — 20.22) × 1.0012 =   79.60 cals
Weight (reduced to *vacuo*) of water run into coil   60.64 gms
Water equivalent of water placed in calorimeter   1276.25 gms
Water equivalent of $1/_2$ the water run into the coil   30.32 gms
Total water equivalent for water   1306.57 gms

$$\text{Water equivalent of calorimetric parts} = \left(\frac{60.64 \times 79.60}{3.572}\right) - 1306.6 =$$

44.7

Five determinations of the water equivalent of the ap-
paratus were made in this manner. The data and results
calculated therefrom appear in the following table:

TABLE III

Weight of water in calorimeter (*vacuo*) Gms	Weight of water delivered to coil (*vacuo*) Gms	True rise in temper- ature of calori- meter °	Temper- ature of boiling water °	Mean temper- ature of calori- meter °	Total water equiv- alent Gms	Water equiv- alent of cal- orimetric parts Gms
1276.25	65.53	3.833	99.36	20.22	1354.6	45.6
1276.25	54.71	3.230	99.46	20.01	1347.3	43.7
1276.25	62.01	3.646	99.45	20.07	1351.5	44.3
1276.25	68.11	3.985	99.69	20.40	1356.8	46.5
1276.25	60.64	3.572	99.72	20.22	1351.3	44.7

Mean = 45.0

This value of 45.0 grams represents the water equiva-
lent of the calorimetric parts when the quartz boiling vessel
is substituted for the quartz vaporizer. Although the two
quartz vessels are nearly alike in size and were immersed
to the same depth they do not have the same water equiva-
lent because of the fact that the boiling vessel was made of

considerably thicker quartz. It was therefore necessary to determine the amount that the quartz played in fixing the value for the total water equivalent. This was accomplished by the electrical method already described. The assembly of apparatus for this purpose was precisely the same as described for the determination of the total water equivalent of the apparatus when the quartz vaporizer was included in the set-up, except that the vaporizer was replaced by the boiling-vessel. The difference between the two total water equivalents of course gave the difference between the water equivalents of the two quartz vessels, or rather the parts of each concerned in making up the total water equivalent in each case, and enables us to correct the values for the water equivalent as obtained by the "hot water method." The data for the determinations and the results of the calculations made therefrom appear in the following table:

TABLE IV

Weight of water in calorimeter (*vacuo*) Gms	Rise in temperature °	Mean temperature of calorimeter °	Voltage drop across heating element	Weight of silver deposited Gm	Total water equivalent Gms	Water equivalent of all calorimetric parts Gms
1376.5	4.670	20.23	35.000	0.8893	1426.1	49.6
1376.5	4.716	20.16	35.000	0.8963	1423.4	46.9
1376.5	2.409	19.03	35.000	0.4586	1425.6	49.1
1376.5	4.222	19.91	35.000	0.8033	1424.9	48.3
1376.5	4.814	20.25	35.000	0.9150	1423.5	47.0
1376.5	4.794	20.27	35.000	0.9124	1425.4	48.9
1376.5	4.810	20.36	35.000	0.9143	1423.5	47.0
1376.5	4.798	20.32	35.000	0.9126	1424.5	48.0

Mean value 1424.6 gms   48.1 gms

Water equivalent of all calorimetric parts when quartz
    vaporizer is included n set-up   46.7 gms
Water equivalent of all calorimetric parts when quartz
    boiling vessel is substituted for vaporizer   48.1 gms

Difference due to substitution of bo ing-vessel for vaporizer   1.4 gms

From this it is evident that the values obtained for the calorimetric parts as determined by the "hot water method" should be diminished by 1.4 grams to get the value for the parts as used in the measurements of heats of vaporization. This gives 43.6 grams as the water equivalent of all calorimetric parts of the system so set up, whereas by direct calculation from the known weights and specific heats, plus the value which had to be added for the quartz vaporizer (as obtained by the electrical method) the value 44.6 grams was found. Since the total water equivalent for the determinations of heats of vaporization is about 1325 grams, the difference in total water equivalent for these determinations as determined by these two methods is about 1 part in 1325, or a difference of about 0.07 percent.

As the "hot water method" is one which would be likely to give slightly low rather than high results, because of the possibility of loss of heat while the water is running from the boiling chamber into the coil below, more reliance is placed in the other method. In the "hot water method," the water flows through a quartz tube about 53 mm long, the upper 30 mm of which is surrounded at all times during the determination with boiling water, 5 mm of which is between the inside and outside walls of the vacuum jacket, and the remaining 18 mm of which is submerged in the calorimeter water. No loss of heat can occur in the first zone of 30 mm, since this is at all times at the temperature of the boiling water, and probably very little occurs in the second narrow zone of 5 mm, while the heat given out in the third zone is all transmitted to the calorimeter water. The only loss of heat therefore takes place in the very narrow zone between the walls of the flask. This loss, however, must be small, since the zone is narrow, the water passes through it very quickly, it is considerably warmed before the water begins to pass through it (by conduction of heat from the boiling liquid above), thus causing the temperature gradient to be reduced, the tube passing through this zone is well silvered, and the space between the walls is highly evacuated. These reasons for the

small loss of heat in this zone undoubtedly account for the really excellent agreement between the two methods, an agreement which is extremely reassuring as to the accuracy of the value for the water equivalent of the heat of vaporization apparatus.

Heats of Vaporization

Having described the changes in detail made in the apparatus for the measurement of heats of vaporization and having discussed the methods whereby the water equivalent of the apparatus was determined, we may now proceed to the measurements of the heat of vaporization themselves.

In the first half of the new series of determinations the temperature of the steam entering the condensing coil was determined from the existing atmospheric pressure; in the latter half the temperature of the steam as it entered the delivery tube was taken with a standardized thermometer capable of being read to $0.01°$. In a number of the determinations in the first half of the series a water-filled manometer was connected with the vaporization chamber. At no time was there ever any change of pressure sufficient to cause an appreciable error in the determination of the temperature of the steam. What little difference there was, never more than a few mm of water pressure, was negative, *i. e.*, the pressure in the vaporization chamber was slightly less than the atmospheric pressure existing at the time This difference in pressure was usually greatest toward the end of the run, and for the greater portion of the experiment was very slight indeed. The difference in pressure was not sufficient to cause an average error of $0.01°$ for the experiment.

Since the vaporizations took place at varying atmospheric pressures, none of which were as great as 760 mm the values obtained at the different temperatures of vaporization had to be corrected to $100°$ in order that they might be plotted. This correction was made by the formula deduced by Henning[1] for the change in heat of vaporization of water with temperature, the formula being

$$L = 94210 \, (365 - t°)^{0.31249} \text{ cals.}$$

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[1] Loc. cit.

In the neighborhood of 100°, the change of heat of vaporization, as determined by this formula, is 0.63 cals$_{15}$. per degree. The values obtained have all been corrected to 100° by this equation, as is shown in the table. The correction usually amounted to about two-thirds of a calorie. The following table shows the data and results obtained for twenty-one determinations of the heat of vaporization of water made at quite different rates of vaporization, all determinations in which the technique was known to be faulty having been excluded from the table.

The accompanying graph (Fig. 4) shows the dependence of the values obtained on the rate of condensation. As was pointed out in the former paper, and discussed at considerable length, there is every reason to believe that the curve should be a linear one; and this conclusion has been verified repeatedly, not only for the heat of vaporization of water but for the heat of vaporization of a large number of other liquids as well, data and results for which will be published in the near future. A straight line drawn through the points plotted shows that the heat of vaporization of a true gram of water at 100° is 539.9 cals.$_{20.5°}$.[1] In terms of the 21° calorie this becomes 539.8 cals., and as the 21° calorie is about 0.9985 times the 15° calorie, in terms of the latter the value is 539.0.

The new value for the heat of vaporization of water is in good agreement with the values obtained with the Harvard apparatus and published in 1911, the value reported at that time being 538.1 cals.$_{15°}$. The difference amounts to 0.16 percent. This difference is undoubtedly attributable to the fact that in the calculations made from the Harvard data, no account was taken of the water equivalent of the small portion of the glass vaporizer which dipped into the calorimeter water. Assuming that this was about two grams, which is a likely figure as the vaporizer was not set quite as

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[1] The correctness of this graph was determined by the method of least squares. Since the curve is linear the equation used was of the form

$$S = \frac{(\Sigma x . \Sigma xy) - (\Sigma y . \Sigma x^2)}{(\Sigma x)^2 - n\Sigma x^2}.$$

TABLE V

Number of run	Weight of water condensed (vacuo)	Time in minutes	Time for one gram	Rise of temperature (corrected)	Total water equivalent (vacuo)	Barometric pressure	Temperature of steam (T°)	Mean temperature of calorimeter (t°)	Heat evolved by cooling one gram of water	Heat of vaporization + heat evolved by cooling	Heat of vaporization of one gram at T°	Correction to reduce to 100°	Heat of vaporization of one gram at 100°
7	10.172	9.25	0.910	4.726	1325.9	734.8	99.06	20.41	78.74	616.01	537.27	—0.59	536.7
10	8.201	8.0	0.977	3.811	1324.9	731.0	98.91	20.85	78.15	615.69	537.54	—0.69	536.8
12	8.611	6.0	0.697	4.004	1325.1	724.5	98.67	21.12	77.64	616.16	538.52	—0.82	537.7
13	8.899	5.0	0.562	4.145	1325.5	724.5	98.67	20.22	78.54	617.38	538.84	—0.82	538.0
14	8.933	4.0	0.448	4.163	1325.3	725.0	98.69	20.30	78.48	617.63	539.15	—0.82	538.3
16	8.982	12.0	1.337	4.165	1325.3	728.4	98.82	20.67	78.24	614.57	536.33	—0.74	535.6
17	8.744	11.0	1.259	4.062	1325.2	738.5	99.20	20.14	79.15	615.61	536.46	—0.50	536.0
18	8.598	13.0	1.513	3.989	1325.1	737.8	99.17	20.53	78.73	614.47	535.74	—0.54	535.2
19	9.689	7.0	0.723	4.510	1325.7	736.0	99.10	20.16	79.03	617.20	538.17	—0.57	537.6
21	9.687	10.0	1.033	4.500	1325.7	747.8	99.55	20.74	78.90	615.70	536.80	—0.28	536.5
23	9.301	4.0	0.430	4.337	1325.5	732.9	98.99	20.10	78.98	618.07	539.09	—0.63	538.5
24	9.122	9.0	0.988	4.237	1325.4	—	99.14	20.70	78.53	615.63	537.10	—0.54	536.6
27	9.528	10.0	1.050	4.428	1325.6	—	99.09	20.23	78.95	616.05	537.10	—0.57	536.5
29	9.612	12.0	1.249	4.459	1325.6	—	99.07	20.42	78.74	614.95	536.21	—0.59	535.6
30	10.507	14.0	1.334	4.867	1326.1	—	99.01	20.34	78.76	614.25	535.49	—0.57	534.9
31	9.734	8.0	0.823	4.522	1325.7	—	98.85	20.58	78.36	615.85	537.49	—0.72	536.8
33	9.498	14.0	1.054	4.413	1325.6	—	99.13	20.48	78.74	615.90	537.26	—0.50	536.7
36	10.103	10.0	1.288	4.681	1325.9	—	98.87	20.60	78.34	614.33	535.99	—0.72	535.3
37	9.911	13.0	1.414	4.596	1325.6	—	98.85	20.18	78.78	614.81	536.03	—0.55	535.3
39	8.387	4.0	0.478	3.909	1325.0	—	99.02	20.73	78.38	617.55	539.17	—0.63	538.5
41	7.858	13.0	1.656	3.639	1324.7	—	98.88	20.82	78.15	613.47	535.32	—0.71	534.6

Mean, 20.5

J. Howard Mathews

low as in the new series (in which it will be remembered that the correction for the quartz was 4.2 grams), the Harvard series would have given the same value as that found in this new series.
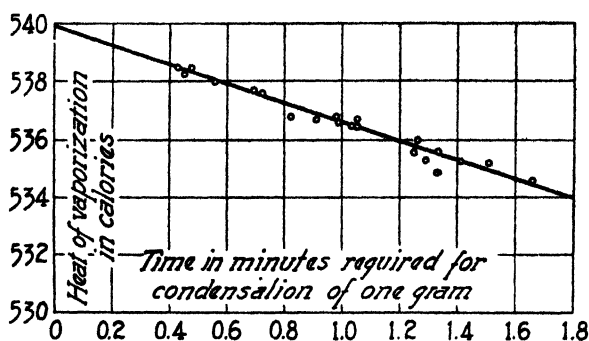
Fig. 4

    The value obtained in the new series is slightly higher than that obtained by Henning, whose electrical method worked out at the Reichsanstalt is probably the best of its class. Henning's value for the heat of vaporization of a true gram of water at 100° is 538.7 cals.$_{15°}$. Inasmuch as the two methods are quite different in principle, one depending on a measurement of the energy required to vaporize a gram of water, while the other depends on the measurement of the energy given out by the condensation of a gram of vapor, the agreement of the two methods, each of which is the most refined of its class, indicates that the true value for the heat of vaporization of a gram of water at 100° has about been reached.

Summary

    1. The method devised by Richards and the writer for the determination of the heats of vaporization of liquids has been improved upon, particularly by the substitution of a vaporizer made of transparent quartz for those made of glass; and by the use of a better type of adiabatic calorimeter.

    2. The water equivalent of the calorimetric system has been determined with accuracy.

3. The amount of heat required to vaporize a true gram of water into a vacuum at 100° has been ascertained to be 539.0 cals.$_{15°}$.[1]

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[1] If the value for the water equivalent of the apparatus as determined by the electrical method be used in the calculations, the value for the heat of vaporization is raised exactly one calorie. On this basis, which may be more nearly correct than the other on account of the uncertainty of the exact specific heats at 20° of the substances composing the calorimetric parts, the heat of vaporization of a true gram of water at 100° is 540.0 cals.$_{15°}$. This agrees well with the value obtained by Smith, which was 540.7.

FERRIC OXIDE AND ALUMINA

BY FRANCIS H. SCHEETZ

In a paper on the yellow color in bricks, Keane[1] showed that this was due to finely divided, anhydrous ferric oxide stabilized by alumina and possibly to some extent by other substances. In the Mars pigments there is enough alumina to keep the ferric oxide from agglomerating while it is in the hydrous state; but not enough to keep the ferric oxide from turning red when all the water is driven off. He concluded that it should be possible to obtain a buff product which would stand heating if one should precipitate a relatively small amount of ferrous hydroxide along with a relatively large amount of alumina. I have made a few experiments to test this point. Mixtures of ferrous sulphate and aluminum sulphate were made up in triplicate so that after oxidation they would contain 2, 3 and 4 parts of Fe_2O_3 per hundred parts of $Fe_2O_3 + Al_2O_3$. These mixtures were dissolved in water and treated, respectively, with sodium carbonate, sodium hydroxide, and calcium hydroxide. Care was taken to make the precipitation complete and to avoid an excess of the precipitants. The precipitates were washed thoroughly by decantation, filtered, and placed in porcelain crucibles. They were dried gradually, heated gradually, and finally blasted at a temperature of about 1000° C. The resulting colors are shown in Table I.

It is quite evident that an anhydrous yellow ferric oxide can be obtained provided agglomeration is prevented. That it is only present consistently where the iron is precipitated with lime water seems to indicate that the calcium serves to stabilize the iron oxide in the yellow form. It may be, however, that the important thing is the dilution of the precipitate with calcium sulphate. This could be tested by starting with ferrous chloride and aluminum chloride instead

[1] Jour. Phys. Chem., 20, 734 (1916).

of with the sulphates. Unfortunately, the time at my disposal did not permit of my making this experiment.

TABLE I

% Fe₂O₃	Precipitated by		
	Na₂CO₃	NaOH	CaO₂H₂
2	Non-uniform product, colored red, pink, pale yellow, and white	Uniform, pinkish white	Uniform, white tinged with yellow
3	Non - uniform, b u ff predominating	Uniform, decided pinkish tinge	Uniform, white tinged with yellow
4	Non-uniform, red and straw-colored	Uniform, pink	Uniform, cream color

Another set of experiments was made to see how the color changed when the percentage of iron was increased and lime water was used as the precipitating agent. The result was a splendid gradation of color as can be seen in Table II.

TABLE II

% Fe₂O₃	Color (precipitation with lime)
2	White with faint yellow tinge
3	White with yellow tinge
4	Cream color
6	Buff
8	Deep buff or light brown
10	Brown
12	Reddish brown
15	Reddish brown
20	Chocolate

Since a yellow-burning clay will turn red before it goes yellow, it should be possible to obtain the same results by starting with the red hydrous ferric oxide. In the preceding experiments the conditions of precipitation do not give the red form directly and consequently the alumina merely has to prevent the agglomeration and is not required to peptize an

Francis H. Scheetz

already agglomerated form. Amounts of ferric chloride and aluminum sulphate were taken which corresponded to the four and six percent mixtures of Table II. The hydrous oxide was precipitated with ammonia and the alumina with calcium hydroxide. The two precipitates were mixed intimately and treated as in the preceding runs. After heating in the blast lamp the resulting color was pinkish gray in both cases, the pinkish tinge being lighter in the one containing less iron. The war prevented further experiments being made.

The conclusions to be drawn from these few experiments are:

1. When lime water is added to a mixture of ferrous and aluminum sulphates, the resulting precipitate is buff colored even after heating to about 1000° C, provided the percentage of ferric oxide in the ferric and aluminum oxides is less than eight.

2. When solutions of ferrous sulphate and aluminum sulphate are precipitated with sodium hydroxide or sodium carbonate, a uniform buff color is not obtained even when there is only two percent of ferric oxide.

3. It is not known whether the important factor is the mere addition of a lime salt or is the presence of calcium sulphate in the precipitate.

4. An anhydrous yellow ferric oxide can be obtained in presence of alumina and calcium sulphate.

Cornell University

CONTACT CATALYSIS. I

BY WILDER D. BANCROFT

General Theory

In 1823 Döbereiner showed that spongy platinum caused hydrogen to ignite in contact with air. While this may seem merely an interesting experiment, the principle involved has led directly or indirectly to such industries as the contact sulphuric acid process, the Hargreaves and Bird salt cake process, the Deacon chlorine process, the Claus sulphur process, the Haber ammonia process, the Ostwald nitric acid process, the process for the hydrogenation of oils, the surface combustion process, and many others. The action of the platinum in accelerating the reaction between hydrogen and oxygen is called catalysis and the phenomenon depends on the adsorption or increased concentration of one or more of the reacting substances at the surface of the catalytic agent.

While most people are willing to speak of adsorption and to let it go at that, attempts have been made to account for adsorption either through the formation of known compounds or of unknown compounds. Rhead and Wheeler[1] discuss the adsorption of oxygen by carbon. "The experiments show that carbon, at all temperatures up to 900° and probably above that temperature, has the power of pertinaciously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but only by increasing the temperature of the carbon during exhaustion. When quickly released in this manner it appears, not as oxygen, but as carbon dioxide and carbon monoxide. The proportions in which it appears in these two oxides when completely removed depend on the temperature at which the carbon has been heated during oxygen-fixation. No physical explanation alone can account for this 'fixation' of oxygen; but, in all probability, it is the outcome of a physico-chemical attraction between oxygen and carbon. Physical,

[1] Jour. Chem. Soc., 103, 462 (1913).

inasmuch as it seems hardly possible to assign any definite
molecular formula to the complex formed, which, indeed shows
progressive variation in composition; chemical, in that no
isolation of the complex can be effected by physical means.
Decomposition of the complex by heat produces carbon
dioxide and carbon monoxide. At a given temperature of
decomposition these oxides make their appearance in a given
ratio. Further, when a rapid stream of air at a given tem-
perature is passed over carbon (which has previously been
'saturated' with oxygen at that temperature) carbon dioxide
and carbon monoxide appear in the products of combustion
in nearly the same ratio as they do in the products of decom-
position of the complex at that temperature. Our hypothesis
is that the first product of combustion of carbon is a loosely
formed physico-chemical complex, which can be regarded as
an unstable compound of carbon and oxygen of an at present
unknown formula C_xO_y. It is probable that no definite
formula can be assigned to this complex....

"For the present it is sufficient to assume that several
carbon molecules hold one oxygen molecule, in bond as it
were, and do not allow it to escape in conjunction with one of
their atoms. A considerable evolution of heat takes place
during this attachment of oxygen molecules, so much so that
some of them eventually acquire sufficient energy to seize
hold of a carbon atom and depart with it as carbon dioxide.
Some of them become torn apart in the process—become
atomized—and leave the carbon molecule as carbon monoxide.
This formation of a complex, and partial decomposition as
fresh oxygen molecules become attached, goes on until the
carbon becomes 'saturated,' the products of combustion during
this period (a comparatively short one) being C_xO_y, CO_2, and
CO. After the carbon has become saturated there is an
alternate formation and decomposition of the complex. Each
molecule that impinges on the carbon is at once seized hold
of to form the complex formed from previous oxygen mole-
cules. So that, finally, when air is passed over saturated
carbon maintained at a constant temperature by the applica-

tion of an external source of heat, carbon dioxide and carbon monoxide appear in the products of combustion in volume sufficient to account for the total volume of oxygen in the air originally passed."

Haber[1] points out that, according to Bragg the ordinary solid crystalline salts are not systems in which one anion and one cation form a molecule which is separated from the next, but that one anion is probably bound to all the surrounding cations. Since there is nothing to show that the outer layer of a crystal differs from the inner portions, there must be forces at the surface of the crystal similar to those acting between the outer layer and the next layer. If we call these forces chemical valences of some sort, it is possib'e that adsorption is due essentially to the saturation of these valences.

This idea has been developed further by Langmuir,[2] who studied the behavior of an electrically heated carbon filament in presence of oxygen at an initial pressure of about 5–10 bars.[3] "These experiments seem to show that when oxygen acts on carbon at, say 1200° K,[4] part of the oxygen reacts to form CO_2, but another part forms an adsorption layer of some sort on the surface which retards the velocity of the reaction. This adsorption layer is probably chemically combined with the carbon, presumably as an extremely stable solid oxide of carbon. · At higher temperatures the rate of formation of this adsorption layer increases rapidly. When a sufficient quantity has accumulated, this compound begins to decompose, forming carbon monoxide, the higher the temperature, the more rapid being the formation of this gas.

"Judging from the great stability of this adsorption layer, which enables it to be heated for half an hour at 2200° K in the highest vacuum without being completely decomposed, a plausible guess as to its constitution is that it consists of oxygen atoms chemically combined with the carbon atoms

[1] Jour. Soc. Chem. Ind., **33,** 50; Zeit. Elektrochemie, **20,** 521 (1914).

[2] Jour. Am. Chem. Soc., **37,** 1139 (1915).

[3] [A bar is the C. G. S. unit of pressure, one dyne/cm². The megabar is one million times this and is almost exactly 750 mm Hg.]

[4] [Absolute temperature on the thermodynamic scale.]

which form the surface of the filament. According to our recent knowledge of the structure of solid bodies, we have the best of reasons for believing that the atoms of solid bodies are held together directly by chemical forces and that a crystal must be looked upon as a single molecule. The carbon atoms in the filament must thus be considered as forming endless carbon chains with each other. It is probably due to the great stability of these carbon chains that carbon has such a low vapor pressure and such a high melting point. In the present case, if we consider the oxygen atom to be chemically combined with one of the outer carbon atoms, we have a structure that could be represented by the formula

$$
\begin{array}{cccc}
O & O & O & O \\
\| & \| & \| & \| \\
C & C & C & C
\end{array}
\quad \text{(oxygen layer)}
$$

$$
\diagdown \diagup \diagdown \diagup \diagdown \diagup \diagdown \quad \text{(body of filament)}
$$

$$
C \quad C \quad C \quad C \quad C
$$
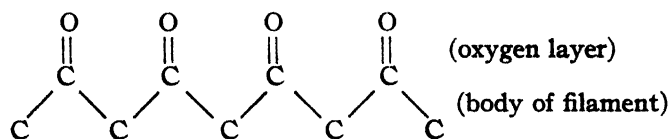
This hypothesis would seem to afford an unforced explanation of the extraordinary difficulty of removing oxygen and hydrogen from carbon.

"Experiments were also made to study the action of the heated carbon on carbon dioxide and monoxide. With carbon dioxide at $1220°$ K no change occurred, but at $1700°$ K carbon monoxide was formed at first slowly and then gradually more rapidly. The total volume, however, usually remained nearly constant, showing that the reaction was not

$$CO_2 + C = 2CO$$

but was rather

$$CO_2 + C = CO \text{ (gas)} + CO \text{ (adsorbed on carbon)}.$$
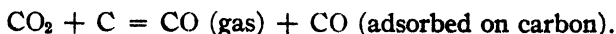
On the other hand, at temperatures up to $2400°$ K, there was never any perceptible change in volume when the filament was heated in carbon monoxide, showing that the adsorbed compound is not formed by adsorption of carbon monoxide.

"The theory of 'molecular layers' leads to a simple but quantitative theory of adsorption. In every reaction that we have studied we have found that, of all the molecules striking

a surface, a large proportion are adsorbed. If the rate of evaporation is high, the molecules will leave the surface very soon, while they may remain a long time if the rate of evaporation is low. The adsorption is due to the fact that a certain time must elapse between the condensation and evaporation of a molecule. In the case of strongly adsorbed bodies, or in all cases where the vapor is nearly saturated, we must take into account the condensation and evaporation in the second and subsequent layers. If we assume that the rate of evaporation in the first layer is different from that for the others, this theory stated mathematically, leads to an equation of the form

$$Q = \cfrac{1}{\cfrac{a}{p} + b - cp}$$

where Q is the amount adsorbed at the pressure p."

In a later paper Langmuir[1] amplifies the conception of compounds due to adsorption. "It is definitely known from the work of Bragg and others that the atoms of crystals are arranged according to space lattices in such a way that the identity of molecules is usually lost. The forces holding the crystal together are thus clearly chemical forces which act probably only between adjacent atoms. On the surface of a crystal, the forces tend to be chemically unsaturated, and atoms or molecules of gases can thus be held firmly by the atoms of the solid.[2] In general the law of multiple combining proportions will apply. Thus each metal atom of the surface will be capable of holding a definite integral number (such as one or two) of atoms of the gas or possibly each two atoms of metal may hold one atom of gas. The atoms held on the surface in this way will form a part of the solid body, being a real continuation of the space lattice of the solid. This layer

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[1] Jour. Am. Chem. Soc., **38**, 1145 (1916).

[2] Haber has suggested, on the basis of Bragg's theory, that adsorption may be the result of unsaturated chemical forces at the surface of a solid body. Haber, however, only considers the force causing adsorption and does not take into account that the amount of adsorption depends on a kinetic equilibrium between the condensation and the evaporation of molecules.

of atoms (or molecules) on the surface may 'be said to be
adsorbed. The surface of the metal is thus looked upon as a
sort of checkerboard containing a definite number N_0 of
spaces per ·square centimeter. Each elementary space is
capable of holding an atom or a definite molecule of adsorbed
gas. The number of elementary spaces, N_0, is probably
usually equal to the number of metal atoms on the surface.
But this is not essential, for we can imagine cases in which
each metal atom holds, for example, two adsorbed atoms or
molecules, so that we should then have twice as many ele-
mentary spaces as metal atoms on the surface."

There are two independent questions involved in Lang-
muir's hypothesis, namely, whether the maximum adsorption
film is only one or two molecules thick and whether this layer
forms a compound with the adsorbing agent. The first may
be true and the second be wrong. Langmuir claims that it
never exceeds two· molecules in thickness for plane surfaces,
though he is apparently willing to concede a greater thickness
for porous substances. There is no question but that the
adsorption film is very thin. Mitscherlich[1] calculates a
thickness of about 0.00005 mm for carbon dioxide adsorbed
by charcoal and the film of water round each particle of clay[2]
is usually assumed to be of the same thickness. It is difficult
to be certain on these points because one does not know the
surface with any degree of accuracy.

When it comes to the question of whether compounds are
formed or not, it must be remembered that Langmuir[3] uses
the word "molecule" in a new sense. He considers that both
solids and liquids consist of atoms held together entirely by
chemical forces. "The conception of the molecules thus al-
most entirely loses its significance except in the case of gases.
In fact we may well look upon any solid or liquid body as
constituting a single large molecule. Any change of phase,
such as the melting of a solid, is thus a typical chemical re-

[1] Sitzungsber. Akad. Wiss. Berlin, 1841, 379.
[2] Cf. Davis: Trans. Am. Ceramic Soc., 16, 69 (1914).
[3] Jour. Am. Chem. Soc., 28, 2222 (1916).

action. The mobility of liquids, according to this viewpoint, is due to a kind of tautomerism." According to this view the oceans and all that in them is constitutes one giant molecule, and catching a fish is a chemical reaction because it breaks up the molecule. This may be perfectly true; but the usefulness of it has not been made clear. For the present, it seems to me much wiser to say that one substance adsorbs another selectively, meaning that the concentration at the surface of the phase has increased. Whenever there is no proof that a compound is formed of the type at present recognized by chemists, it is safer not to postulate the existence of compounds. If the time ever comes when it is a distinct advantage to distinguish an entirely new type of compound, that can be done; but hopeless confusion will arise whenever a man uses a word in one sense and his listeners in another.

In some cases compounds are undoubtedly formed. Thus when platinum takes up oxygen, a portion of the oxygen is certainly present as oxide. On the other hand, it seems improbable that it would be so difficult to make carbon tetrachloride if the chlorine which is adsorbed by charcoal and thereby made active[1] consisted of a compound of carbon and chlorine. While the oxidizing action of platinum may be due to a platinum oxide, this cannot be true in the case of charcoal and oxygen. Calvert[2] showed that oxygen adsorbed by charcoal will oxidize ethyl alcohol to acetic acid and ethylene to carbon dioxide and water, reactions which certainly cannot be due to any known oxide of carbon.

The increased concentration at the surface of a solid will necessarily cause an increase in reaction velocity as a result of adsorption quite apart from any special catalytic action which the solid may exert. There may be catalytic action in in all cases; but in some there must be, so it will be better to consider a few cases in which the results may perhaps be due solely to increase of concentration and we can then take up the more interesting cases in which catalysis must occur.

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[1] Damoiseau: Comptes rendus, **73**, 60 (1876).

[2] Jour. Chem. Soc., **20**, 293 (1867).

Döbereiner showed that when hydrogen is allowed to pass over spongy platinum in presence of air, the hydrogen takes fire. So far as I know, nobody has ever compressed oxy-hydrogen gas so that it occupied the volume of liquid water. If no combination took place under these circumstances, it would be necessary to ascribe a special catalytic action to the platinum. Until that experiment is tried, it is possible that the adsorbed hydrogen reacts with the adsorbed oxygen or with platinum hydroxide by virtue of the increase in con-centration. In the case of SO_2 and O_2, Hempel[1] obtained a yield of 65 percent SO_3 without any catalytic agent by working at a pressure of 30–40 atmospheres. On the other hand the fact that charcoal has practically no effect in causing hydrogen and oxygen to combine indicates that some other factor is important in addition to increased surface concentration.

The more interesting cases of contact catalysis are those in which we know that some other factor enters besides that of increased concentration. If a given substance decomposes in one way in presence of one catalytic agent and in another way in presence of a different catalytic agent, the difference in the reaction products cannot be explained on the hypothesis of increased surface concentration. Since we have selective ad-sorption from a gaseous mixture, we may also have selective adsorption of the reaction products and this may cause one reaction to predominate at the expense of another.

It is usually assumed that a catalytic agent cannot dis-place the equilibrium and the reason for this is given clearly by van't Hoff.[2] "Theoretically too, assuming that contact actions affected the equilibrium, we should come upon a *perpetuum mobile*, by working alternately with and without the contact substance; the conversion might thus be carried backward and forwards indefinitely, and so work might be accomplished in any way, without fall of temperature in contradiction to the laws of thermodynamics." Nernst[3] takes

[1] Ber. deutsch. chem. Ges., **23**, 445 (1890).
[2] "Lectures on Theoretical Physical Chemistry," 215 (1898).
[3] "Theoretical Chemistry," 617 (1916).

the same view, as does practically everybody else. "The catalyst cannot of course affect the affinity of a process. To do so would be in contradiction to the second law of thermodynamics, according to which the affinity of an isothermal process, as measured by the maximal work, depends only on the initial and final states. The activity of the catalyst therefore does not touch the driving force of a reaction but only the opposing resistance, as was early recognized.[1] Since the catalyst takes no part in the reaction, the equilibrium constant is not altered by its presence. This was seen to be equal to the ratio between the velocity constants of the two reactions in opposite signs. *A catalyst must therefore always affect the velocity of the reverse reaction.* If, for example, any added substance increases the rate of formation of the body it must equally increase its velocity of decomposition. We find an example of this in the known fact that the presence of acids causes both the formation and the saponification of esters to take place with increased velocity. The observation of Baker that in absence of water vapor, gaseous ammonium chloride does not dissociate, and on the other hand dry ammonia does not combine with hydrochloric acid may be explained in the same way."

I trust that I have the proper respect for the laws of thermodynamics; but there is always the possibility that something has been overlooked and that the laws of thermodynamics have not been applied properly. Neither van't Hoff nor Nernst is considering the case where the reaction takes place immeasurably slowly in one phase. They are also not considering the possibility of a solvent acting as a catalytic agent.

Ostwald[2] says that "when a substance by its mere presence alters the velocity of a reaction, and may be recovered unaltered in nature or amount at the end, it is called a catalytic

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[1] See for instance Helmholtz: "Die Erhaltung der Kraft," 25.

[2] Zeit. Elektrochemie, **7**, 998 (1901); Lehrbuch allgem, Chemie, **2** II, 248 (1902). Quoted from Bigelow: "Theoretical and Physical Chemistry," 365 (1912).

agent or catalyzer, and the phenomenon is called catalysis."
Nernst's[1] defin tion is practically identical, being based on
Ostwald's. Catalysis "means an increase in velocity of re-
action caused by the presence of substances which do not
take part in it (or only to a secondary extent), although the
reaction is capable of taking place without their presence."
Since a solvent changes the reaction velocity without neces-
sarily taking part in the reaction, a solvent may be considered
as a catalytic agent. This is recognized explicitly by Ost-
wald.[2]

"Catalysis, as just defined, is an uncommonly wide-
spread phenomenon, which actually occurs in all cases in
which the rate of a chemical reaction can be measured. A
splendid example of this is to be found in the well-known
experiments of Menschutkin. For a number of different
reactions he has proved that the reaction velocity may vary
within wide limits depending on the solvent used. We must
therefore call these actions of the solvents catalytic actions.
This characterization does not of course exclude the possi-
bility that it may be shown that compounds are formed be-
tween the solvents and the reagents so that the changes in
reaction velocity can be referred to changes in the active
masses. All intermediate stages can be found between cases
like these and cases in which a very small amount of an added
substance changes the reaction velocity very much. This
latter class of cases is the only one that hitherto has been
considered as catalysis; but the difference is merely a quan-
titative one and it is improper, when studying these things
systematically, to exclude those cases in which the acceleration
is relatively small."

Bigelow[3] says practically the same thing in somewhat
different words. "Instances of catalysis may be multiplied
almost without number. A given reaction occurs at different
rates in different solvents. The solvent remains unaltered

[1] "Theoretical Chemistry," 590, 616 (1916).
[2] Zeit. Elektrochemie, 9, 998 (1901).
[3] "Theoretical and Physical Chemistry," 366 (1912).

at the end of the reaction and hence all the effects must be reckoned with catalytic actions. Menschutkin[1] measured the velocity of the reaction

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$$

in a variety of solvents. In hexane the velocity constant k had the value 0.000180; in heptane, 0.000235; in benzene, 0.00584; in ethyl alcohol, 0.0433; in benzyl alcohol, 0.133; and intermediate values in other solvents. The velocity is nearly one thousand times as great in benzyl alcohol as in hexane.

"The difference in velocity of the above reaction in hexane and heptane is but slight, though the quantity of the catalytic agent is large, it being the solvent. The most fascinating instances of catalysis are those in which small traces of the catalyzer produce great effects, and we are rather too apt to assume that these alone are instances of catalysis. Some of the quantitative measurements are indeed striking. For instance, Bredig,[2] studying the increased velocity with which hydrogen peroxide decomposes in the presence of colloidal platinum, was able to detect such increase when the concentration of the platinum was but one senventy-millionth of a symbol weight per liter. Again Titoff[3] found that the velocity with which sodium sulphite was oxidized was increased 30 percent by the presence of one-thousandth of a formula weight in grams of copper sulphate per liter."

The effect of the solvent on the rate of decomposition of xanthogenic acid into carbon bisulphide and alcohol has been studied by von Halban and Kirsch.[4] The reaction may be written $HSSCOC_2H_5 = CS_2 + C_2H_5OH$. If the reaction velocity constant for carbon bisulphide as solvent be taken as unity, we get the following values at $25°$: carbon bisulphide, 1.00; ligroin (hexane), 1.50; chloroform, 3.64; benzene, 5.15; nitrobenzene, 315; ether, 485; acetone, 25980; alcohol,

[1] Zeit. phys. Chem., **6**, 41 (1890).
[2] Ibid., **31**, 258 (1899).
[3] Ibid., **45**, 641 (1903).
[4] Ibid., **82**, 325 (1913).

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1,000,000. In other words, the decomposition takes place a million times as rapidly in alcohol, as in carbon bisulphide, the two decomposition products.

It is well known that a solvent·may displace equilibrium. Cundall[1] has made a quantitative colorimetric study of solutions of N_2O_4 in different solvents at concentrations of nearly 3 grams N_2O_4 per 100 cc. Ostwald's calculations[2] of these data are given in Table I. The percentage dissociation varies for the extreme cases in the ratio of about one to six. The dissociation in the vapor would be much greater for the same concentrations than in any of the liquids, for Ostwald calculates that the dissociation constant for the gas is about one hundred times that for nitrogen peroxide in chloroform at 20° and about four hundred times that for nitrogen peroxide in chloroform at 0°. No actual measurements have been made on nitrogen peroxide vapor at the corresponding pressures of 6–7 atmospheres.

TABLE I

Dissociation of N_2O_4 in Solution

Solvent	Liters per mol	Percentage dissociation		
		10°	20°	30°
Chloroform	3.36	0.36	0.58	1.24
Methyl chloride	3.39	0.29	0.56	1.06
Carbon tetrachloride	3.48	0.46	0.82	1.43
Ethylene chloride	3.45	0.20	0.41	0.70
Ethylidene chloride	3.13	0.32	0.60	1.09
Benzene	3.33	0.22	0.43	0.80
Chlorbenzene	3.40	0.30	0.56	0.99
Brombenzene	3.22	0.31	0.55	0.94
Bromoform	3.39	0.23	0.52	0.98
Ethyl bromide	2.93	0.33	0.63	1.14
Ethylene bromide	3.34	0.37	0.59	0.95
Silicon tetrachloride	3.34	0.71	1.22	2.43
Carbon bisulphide	3.20	0.57	1.05	1.79
Acetic acid	3.25	0.11	0.22	0.40

[1] Jour. Chem. Soc., **59**, 1076 (1899); **67**, 794 (1895).
[2] Ostwald: Lehrbuch allgem. Chemie, **2**, II, 602 (1892).

An even more striking case is that of hydrochloric acid and water where there are practically no ions in the vapor phase and the hydrochloric acid is highly dissociated in the liquid phase. As Nernst[1] points out, "the assumption that water has an exceptional power of causing dissolved substances to dissociate electrolytically can be replaced by another that the solubility coefficients of ions in water is exceptionally large. Possibly this latter assumption may seem less abhorrent to some than the first one; but the one is merely another way of wording the other." The general effect of the solvent in displacing equilibrium is to cause a greater relative formation of the system which is the more soluble in the solvent.

In the case of nitrogen peroxide and a solvent, we get one equilibrium in the vapor and another equilibrium in the solution; but if we had a hypothetical case in which the reaction took place immeasurably slowly in the vapor phase and relatively rapidly in the solution, the equilibrium in the vapor would be reached only by volatilization from the solution and this might give rise to some rather interesting results. This has been discussed to some extent by Ostwald,[2] who, however, apparently never saw the possible consequences of his argument.

"It is a general phenomenon that all gas reactions take place relatively very slowly. This important fact appears for instance clearly in the experiments of Berthelot and Péan de St. Gilles. The formation of ester from acid and alcohol was compared at the same temperature in two experiments, in one of which the substances were liquid and in the other of which the substances were present as vapors. Although the experiments do not enable us to tell accurately whether the decrease in reaction velocity is due solely to the decrease in the concentration or whether, as seems more probable, the decrease in reaction velocity is greater than that calculated on this assumption, they suffice to show that the reaction

[1] Zeit. phys. Chem., **8**, 139 (1891).
[2] Zeit. Elektrochemie, **7**, 1002 (1901).

velocity drops to about one thousandth as one passes from the liquid to the vapor phase.

"On this we may base a theory of catalytic accelerations (Bodenstein). Let us imagine that a portion of a gaseous system is converted at the same temperature into the liquid state or is given a density comparable with that of the liquid state. The reaction will take place more rapidly in this portion and the liquefied reacting substances will change into the corresponding reaction products. If the cause for the liquefaction or for the increase in density is such that more of the reacting substances are liquefied or given an increased density as fast as the preceding portions have reacted, these would react rapidly and the process would be repeated, with the result that we have an accelerated reaction. Such an action of platinum on gases is quite conceivable. I do not mean by this to say that this is the way that platinum catalyses actually occur but merely to point out a possible way in which they might occur. This would then be the simplest case of the accelerating intermediate reactions to which I have previously referred.

"Professor Bredig has recently pointed out to me that the mechanism of such an acceleration becomes intelligible if we consider a liquid medium in which is suspended a small drop of a second liquid. If this suspended liquid has the property of making the substances dissolved in it react more rapidly than in the main mass, the bulk of the reaction will take place there. The reaction products will diffuse into the outer liquid and new portions of the reacting substances will diffuse into the drop. In this way practically all of the reacting substances will diffuse into the suspended liquid and will react there, the result being an acceleration of the reaction.

"According to Bredig, what has been outlined here may perhaps be applicable to the case where the catalytic agent is present in the colloidal state in the liquid. It is known that Professor Bredig and his pupils in a series of splendid investigations have shown and measured the manifold and energetic catalytic actions due to colloidal platinum and other

colloidal metals prepared by the Bredig process. He has also emphasized repeatedly that the enzymes, those natural and very effective catalytic agents, are also always in a state of colloidal solution or suspension.

"These considerations have no claim to being anything more than suggestions which can be tested experimentally. I cannot refrain from pointing out that it has only been possible to make suggestions which can be tested scientifically, since we adopted the conception of a catalytic agent being an accelerator. Let one just try to do anything like this on the assumption of molecular vibrations."

The same matter has been discussed by Höber.[1] "When ethyl acetate is dissolved in benzene, it does not change perceptibly with time.[2] If one adds an aqueous acid solution as a ferment, the catalytic decomposition takes place. Bredig,[3] who first developed the point of view, devised the following artificial enzyme action; When triethylamine is added to a solution of methyl acetate in benzene at 25°, the base does not saponify the ester under these conditions. If one forms an emulsion by shaking the mixture with 2.5 percent water, the base and the ester dissolve freely in the water as the better solvent and the ester is saponified rapidly by the base which is highly dissociated in water. The drops of water therefore act as an enzyme, increasing the reaction velocity without themselves taking part appreciably in the reaction. In this way we gain a conception of the way in which catalytic agents act which is quite different from the ordinary point of view. The enzyme does not combine with the substrate to form an intermediate product in an intermediate reaction, but owes its catalytic action to its being a better reaction medium."

Neither Ostwald nor Bredig has drawn the important corollary that the equilibrium will be determined primarily by the solvent in which the reaction takes place and that it is therefore theoretically possible to obtain one set of reaction

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[1] Physikalische Chemie der Zelle und der Gewebe, 4th Ed., 703 (1914).

[2] [It is not clear from this statement what reaction Höber has in mind.]

[3] "Anorganische Fermente," 92 (1901).

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products with one liquid as catalytic agent and another set of reaction products with another liquid as catalytic agent.

If we consider a solid catalytic agent as equivalent to a drop of liquid, as suggested by Bredig, and the formation of an adsorption film as equivalent for our purposes to solution, it becomes possible theoretically to get different reaction products with different solid catalytic agents just as it is possible theoretically to get different reaction products with different solvents. If we have a reaction which takes place extremely slowly in the vapor phase and relatively rapidly in or at the surface of a solid catalytic agent, we shall get the equilibrium in or at the surface which corresponds to that solid catalytic agent hypothetically as equivalent to a solvent. This equilibrium will not necessarily be the same as the theoretical equilibrium in the vapor phase any more than the dissociation of nitrogen peroxide in chloroform solution is the same as the dissociation of nitrogen peroxide in the vapor phase. When the reaction products diffuse from the surface of the solid catalytic agent into the vapor phase, they do not react in measurable time by definition, and consequently we get in the vapor phase an apparent equilibrium corresponding to that at the surface of the solid catalytic agent and therefore varying perhaps with different solid catalytic agents.[1]

The conception of a solid catalytic agent as being equivalent to a drop or film of liquid is due originally to Bredig[2] and has also been made use of by Bodenstein,[3] who considers the reacting substances as actually dissolved in the platinum instead of adsorbed at the surface. In so far as the platinum is actually a solvent and not merely equivalent to a solvent, the possibility of an apparent displacement of equilibrium is beyond question and the alleged violation of the second law of thermodynamics becomes an imaginary one.

We have now to consider what the direction of the reaction will be when several reactions are possible. We have

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[1] Cf. Bancroft: Jour. Phys. Chem., **12**, 138 (1908).
[2] Zeit. Elektrochemie, **7**, 1002 (1901).
[3] Zeit. phys. Chem., **46**, 736 (1903).

already seen that the solvent displaces the equilibrium so that the ratio of the more soluble system to the less soluble system in the solution is increased. This can be put in a more general form which covers all cases by saying that there is a relative increase in the amount of the system, the chemical potential of which is decreased relatively by the medium.[1] If one treats a substance with a dehydrating agent, the tendency of the substance to split off water is increased. A very interesting case coming under this general head is the decomposition of hydrazine in hot aqueous solution in presence of platinum.[2] Hydrazine may decompose in three different ways according to the reactions

$$6N_2H_4 = 8NH_3 + 2N_2$$
$$6N_2H_4 = 6NH_3 + 3N_2 + 2H_2$$
$$6N_2H_4 = 4NH_3 + 4N_2 + 6H_2.$$
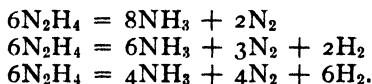
The first reaction is the chief one when starting with hydrazine sulphate; the second one predominates when starting with free hydrazine, while the third one comes to the front in an alkaline hydrazine solution. There is more ammonia formed, the more acid the solution is. This illustration is given as being both typical and simple. Tanatar[3] found that a hot alkaline solution of hydroxylamine decomposed chiefly according to the equation $3NH_2OH = NH_3 + N_2 + 3H_2O$, while the same solution in presence of platinum decomposed according to the equation $4NH_2OH = 2NH_3 + N_2O + 3H_2O$. The change in the course of the reaction is due to the addition of the solid catalytic agent and not to any change in the alkalinity or acidity. Tanatar considers that part of the hydroxylamine oxidizes the platinum to an unspecified oxide, being itself reduced to ammonia, while the platinum oxide then oxidizes another portion of the hydroxylamine to nitrous oxide. This explanation seems absolutely impossible and it will probably be wise not to offer any explanation for this case until more is known about the adsorption of nitrous oxide by platinum.

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[1] Cf. Miller: Jour. Phys. Chem., **1**, 636 (1897).

[2] Tanatar: Zeit. phys. Chem., **40**, 475; **41**, 37 (1902).

[3] Zeit. phys. Chem., **40**, 475 (1902).

Displacements of equilibrium by adsorption are perfectly familiar matters.   If fuller's earth be shaken with water and then filtered, the filtrate is neutral to litmus paper[1] or to phenolphthalein, showing that no soluble base or acid is present.   If fuller's earth be shaken with a sodium chloride solution and filtered, the filtrate is acid to litmus or to phenolphthalein.   This is because fuller's earth has adsorbed the base, thereby leaving an excess of acid in the solution.

Freundlich and Masius[2] have studied the adsorption of aniline benzoate and aniline acetate by charcoal.   It so happens that aniline is adsorbed less strongly than benzoic acid by charcoal and more strongly than acetic acid.   From a solution of aniline benzoate charcoal therefore adsorbs more benzoic acid than aniline, while more aniline than acetic acid is adsorbed from an aniline acetate solution.

Silk has such a marked selective adsorption for rosaniline that it will not only decompose the hydrochloride, leaving the acid behind; but it will convert the carbinol base back into the color base in presence of an excess of ammonia,[3] the silk being dyed red from a colorless ammoniacal solution.   The displacement of equilibrium is in or on the silk phase and not in the solution.   Another, though less striking, experiment with silk and rosaniline has been carried out by Mills.[4]   "At the heat of boiling water a solution of rosaniline hydrochloride or acetate undergoes more or less complete dissociation, attended, of course, by loss of color.   Thus, for example, if a solution of either of these salts, containing 0.0000003 g. in 1 cc [three-tenths of a milligram per liter] be boiled for half an hour, complete decoloration ensues.   But a piece of purified silk, immersed in this liquid, is almost immediately dyed red. We thus have the remarkable phenomenon, admirably suited to illustrate dissociation for a lecture, of silk being dyed red with a colorless solution of magenta."

[1] Cf. Cameron: Jour. Phys. Chem., **14,** 400 (1910).

[2] Van Bemmelen Gedenkboek, 100 (1910).

[3] Jacquemin. Comptes rendus, **82,** 261 (1876).

[4] Jour. Chem. Soc., **35,** 27 (1876).

We are now in a position to predict that, when we are dealing with something more than a mere increase in concentration, we may get different reaction products with different catalytic agents. Under these circumstances the nature of the reaction will be determined by the specific adsorption of the reaction products by the catalytic agent in question.

When heated in presence of certain catalytic agents alcohol may be decomposed into aldehyde and hydrogen or into ethylene and water, to take two instances. We should expect catalytic agents which adsorb hydrogen strongly to cause the splitting to aldehyde and hydrogen while catalytic agents which adsorb water readily should promote the decomposition into ethylene and water. As a matter of fact alcohol is decomposed nearly quantitatively into aldehyde and hydrogen when passed over heated nickel, which adsorbs hydrogen.[1] It is decomposed nearly quantitatively into ethylene and water when passed over heated alumina,[2] which must therefore adsorb water. Johnson[3] has shown that up to a certain point alumina adsorbs water so completely that phosphorus pentoxide takes no more out. When titanium oxide is used as the catalytic agent, both reactions take place simultaneously, and a yield of 84 percent ethylene and 16 percent hydrogen can be obtained under certain conditions. This would seem to imply that titanium oxide adsorbs both water and hydrogen. This was proved indirectly by Mr. Engelder in the Cornell laboratory. When aqueous alcohol is passed over titanium oxide, the water vapor cuts down the reaction which produces water and consequently the relative yield of acetaldehyde is increased over that obtained from absolute alcohol. When hydrogen is mixed with the alcohol vapor, the relative amount of ethylene is increased. A some-

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[1] Sabatier and Senderens: Comptes rendus, **136**, 738, 921, 936, 983 (1903).

[2] Ipatieff: Ber. deutsch, chem. Ges., **34**, 3579 (1901); **35**, 1047, 1057 (1902); **36**, 1990, 2003, 2014, 2016 (1903).

[3] Jour. Am. Chem. Soc., **34**, 911 (1912).

what similar result appears to have been obtained uncon-
sciously by Berthelot[1] nearly fifty years ago. He heated
formic acid at 260° without any specified catalytic agent and
found that when only a third of the formic acid is decomposed
the reaction appears to be $HCO_2H = CO + H_2O$. If all the
formic acid is decomposed, the reaction is approximately
$2HCO_2H = CO + H_2O + CO_2 + H_2$. This unexpected re-
sult can only be true in case the reaction $HCO_2H = CO_2 + H_2$
predominates during the latter part of the decomposition and
this can happen only in case the original decomposition prod-
ucts check the initial reaction and thus permit the second
reaction to come to the fore. It was this unexplained ob-
servation by Berthelot which gave me the clue to the present
theory of contact catalysis.

When acetaldehyde and excess of hydrogen are passed
over suitably heated nickel, the reaction is reversed and
alcohol is formed. Similarly benzene and an excess of hy-
drogen forms cyclohexane in presence of nickel and nickel
splits cyclohexane into benzene and hydrogen.[2] We can even
go one step farther and can convert either benzene or cyclo-
hexane into methane by treating with nickel and a sufficient
excess of hydrogen. Zelinsky[3] has shown that palladium will
split cyclohexane into benzene and hydrogen or will reverse
the reaction under different conditions. Since the tem-
peratures are different with palladium and with nickel, it is
evident that we have a true displacement of equilibrium
though no quantitative study has yet been made. Wil-
stätter and Hatt[4] have shown that when benzene is dissolved
in cold acetic acid it can be converted into cyclohexane by the
action of hydrogen in the presence of platinum black.

It is interesting to note that Jellinek[5] claims to have
obtained more ammonia than corresponds to equilibrium

[1] Ann. Chim. Phys., (4) 18, 42 (1869).
[2] Sabatier and Senderens: Ann. Chim. Phys., (8) 4, 336, 361 (1905).
[3] Ber. deutsch. chem. Ges., 44, 3121 (1911).
[4] Ibid., 45, 1471 (1912); cf. Willard: Ibid., 45, 2615 (1912).
[5] Zeit. anorg. Chem., 71, 121 (1911).

conditions by heating nitrogen and hydrogen in presence of iron as catalytic agent. He points out that iron adsorbs ammonia very markedly. It is therefore theoretically possible that his data are correct, though they would have to be repeated before one would dare to lay much stress on them. Müller[1] electrolyzed a normal potassium nitrate solution using a porous diaphragm, a platinum anode 2 cm × 5 cm and a cathode of the same size made of platinum, iron, or zinc. The cathode solution was stirred by a current of hydrogen. A current of one ampere was sent through the cell for three hours. In Table II are given the metal used as cathode, the voltage drop at the terminals, and the amount of ammonia formed.

TABLE II

Cathode metal	Voltage drop	Grams Ammonia
Smooth platinum	4.8	0.0416
Iron	4.4	0.1894
Zinc	4.5	0.1210

Müller himself comments on the fact that most ammonia was formed at the iron cathode although the voltage drop was lowest in this case. It is probable, though not proved, that this is a catalytic action of the iron cathode and dependent on the adsorption of ammonia by iron.

The catalytic setting free of hydrogen has been studied by Sieverts[2] for the case of hypophosphorous acid. In aqueous solutions platinum, silver, and copper cause hypophosphorous acid and phosphorous acid to split off hydrogen, the final products being phosphorous acid and orthophosphoric acid, respectively, while the intermediate products are presumably metaphosphorous acid and metaphosphoric acid, respectively. The reactions may be written

$$H_3PO_2 + H_2O = HPO_2 + H_2O + H_2 = H_3PO_3 + H_2$$
$$H_3PO_3 + H_2O = HPO_3 + H_2O + H_2 = H_3PO_4 + H_2.$$
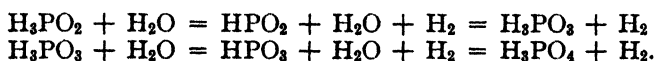
[1] Zeit. anorg. Chem., **26**, 43 (1901).
[2] Ibid., **64**, 59 (1909); **76**, 1 (1912). Zeit. phys. Chem., **91**, 199 (1916).

It is the natural thing to do to consider the production
of formaldehyde from methyl alcohol in presence of platinum
as a plain case of limited oxidation of methyl alcohol; but
there seems now to be no question but that the real reaction[1]
is undoubtedly a catalytic splitting of methyl alcohol into
formaldehyde and hydrogen, the nascent hydrogen then re-
acting with oxygen, which latter therefore really acts as a
depolarizer. It is probable, though not proved, that the
oxidation of alcohol to acetaldehyde by osmium tetroxide[2]
may involve a catalytic dissociation as a first step.

An interesting case of the splitting-off of hydrogen is the
conversion of alcohol into acetic acid by means of hot soda-
lime. The reaction is usually written $CH_3CH_2OH + NaOH =$
$CH_3CO_2Na + 2H_2$; but Mr. Carroll has found that the reaction
takes place in several stages.

$$CH_3CH_2OH + NaOH = CH_3CHO + NaOH + H_2O =$$
$$CH_2CO + NaOH + 2H_2 = CH_3CO_2Na + 2H_2.$$
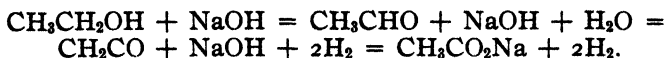
The caustic soda is the catalytic agent and the lime is prac-
tically inert at the temperatures in question.

The catalytic action of caustic alkalies accounts for the
fact that hydrogen is so often evolved when organic com-
pounds are fused with alkalies.[3] Thus oleic acid reacts with
fused caustic potash to form potassium palmitate, potassium
acetate, and hydrogen[4] according to the equation

$$C_{17}H_{33}CO_2H + 2KOH = C_{15}H_{31}CO_2K + CH_3CO_2K + H_2.$$

In order to cut down the reducing action of the nascent hy-
drogen it may even be necessary to add an oxidizing agent as
in the production of alizarine from anthraquinone sulphonic
acid.

It hardly seems probable that this evolution of hydrogen
should depend on the organic substance forming a second
liquid layer with fused alkali, and yet, if not, we pass direct

[1] Cf. LeBlanc and Plaschke: Zeit. Elektrochemie, **17**, 471 (1911).

[2] Hofmann: Ber. deutsch, chem. Ges., **46**, 1657, 2854 (1913).

[3] Lassar-Cohn: "Arbeitsmethoden für organisch-chemische Laboratorien," 264 (1903).

[4] Varrentrapp: Liebig's Ann., **35**, 196 (1840).

from catalytic action in heterogeneous systems to catalysis in homogeneous systems. In presence of cuprous oxide and alkali, formaldehyde gives off hydrogen[1] according to the equation $HCHO + NaOH = HCO_2Na$. This is clearly a catalytic splitting-off of hydrogen in presence of cuprous oxide. If we leave out the cuprous oxide the reaction becomes $2HCHO + NaOH = HCO_2Na + CH_3OH$. This is usually described as simultaneous oxidation and reduction; but it is really a case of dissociation, the nascent hydrogen reducing some of the formaldehyde to methyl alcohol. If we have present a substance which is reduced more readily than formaldehyde, such as sodium peroxide, the reaction is of course slightly different[2] and may be written

$$2HCHO + Na_2O_2 = 2HCO_2Na + H_2O + H_2.$$

One does not like to talk about adsorption in homogeneous systems and I think it would be undesirable to try to formulate now a theory of catalysis in homogeneous systems. I do wish, however, to call attention to part of what Nernst says about electrostriction by free ions.[3]

"It is very remarkable that the values for the change of volume of dissociated substances [dissolving in water] are extraordinarily small, being considerably smaller than the molecular volume of the solid substance. In some cases (*e. g.*, sodium carbonate, magnesium sulphate, zinc sulphate) they are even negative. It seems, therefore, that with increasing separation of ions, the change of volume has in general a marked tendency to fall off; this may be seen clearly from the exact measurements of Kohlrausch and Hallwachs. The effects hitherto observed can be explained most easily by supposing the *solvent water to be strongly contracted by the presence of free ions*. It is of interest to know that such a contraction might be expected from the electric charges of the ions; every electric liquid must suffer a contraction if, as

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[1] Loew: Ber. deutsch. chem. Ges., **20,** 144 (1887).

[2] Frankforter and West: Jour. Am. Chem. Soc., **27,** 714 (1905).

[3] Nernst: "Theoretical Chemistry," 420 (1916).

usually happens, the dielectric constant increases with pressure. It is therefore natural to suppose that the observed contraction of water by dissolved electrolytes is due to the electrostatic field of the ions; the theory of this electrostriction by free ions has been developed by Drude and Nernst.[1] This electrostriction, which, according to firm physical principles, must always be present, causes therefore a contraction of the solvent; the increase in internal pressure thus brought about will not be distributed equally over the whole solvent but on the contrary will be very great in the immediate neighborhood of each ion, where a strong potential gradient exists, and will fall off rapidly at a short distance away. In many respects, however, the solvent will behave as if it were evenly subjected to a higher pressure. In this way we arrive at a very simple physical interpretation of the internal pressure of solutions."

Kohlrausch[2] has also emphasized the idea that there is a shell of water round an ion, which differs to some extent from the rest of the water. Kohlrausch makes the following hypotheses: "About every ion moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ion. The atmospheres of multivalent or compound ions differ from those of monatomic ions. Data are at present lacking for a more complete representation. The electrolytic resistance of an ion is a frictional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent diminishes as the atmosphere becomes of greater thickness." One of the conclusions drawn by Kohlrausch from these premises and from the data is as follows: "I now come to the remarkable relationship between the mobility of the ions and their temperature coefficients. This first led me to seek a general explanation for the electrolytic resistance in the idea of a water atmosphere, in order to escape being compelled to explain this otherwise unreconcilable funda-

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[1] Zeit. phys. Chem., **15,** 79 (1894).

[2] Proc. Roy. Soc., **71,** 338 (1903).

mental characteristic of the ions as a *deus ex machina.* Assuming as the single fundamental characteristic of each univalent monatomic ion the formation of a water atmosphere, which varies according to the nature of the ion, the mobility of the complex on the one side, and its temperature coefficient on the other, will be functions of the atmospheric formations, and therefore both quantities must hold functional relations to each other. We know too little of the molecular forces at present to attempt to describe this connection more exactly. But for the case in which the water shell is so thick that the ion exerts no force beyond it, the resistance to motion becomes simply a matter of water friction, which explains the fact that the most sluggish ions have nearly the same temperature coefficients as the viscosity. In the case of smaller aggregations, we must remain content with the fact that we have at least the possibility of a fundamental explanation."

If one admits the existence of special water films around the ions, all gradations between heterogeneous and homogeneous systems become possible. It opens up all sorts of fascinating possibilities; but now is not the time to discuss them.

Coming back to definite cases of contact catalysis, there are several instances which perhaps call for a word of comment. In all such cases as the decomposition of arsenic hydride, antimony hydride, etc., the reaction takes place practically completely at the surface of the containing vessel and not in the mass of the gas. To take a single case, the rate of decomposition of antimony hydride is accelerated by the presence of metallic antimony [1] If we assume that antimony adsorbs antimony or tends to make antimony vapor condense upon it, the catalytic action follows at once. Another case which also belongs in this class is the decomposition of silver oxide into silver and oxygen. Lewis[2] has shown that this reaction is accelerated by silver. At first

[1] Stock and Guttmann Ber deutsch chem Ges, **37**, 901, Bodenstein: 1361 (1904).

[2] Zeit phys Chem, **52**, 310 (1905)

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sight this looks like the catalytic decomposition of one solid
by another; but it seems impossible that the silver should act
at a distance. It is probable therefore that we are really
dealing with the decomposition of silver oxide vapor, in which
case the reaction differs only in degree from the decomposition
of stibnine.

Taylor and Hulett[1] have shown that the decomposition
of mercuric oxide is facilitated by finely-divided platinum,
ferric oxide, manganese dioxide, and cadmium oxide, but not
by stannic oxide or alumina. While this is undoubtedly an
adsorption phenomenon, the details are not sufficient to
enable one to account satisfactorily for the results.

Since Sabatier has done an enormous amount of ex-
perimental work on contact catalysis, we must take his
theoretical views into account even though one does not
agree with them. Sabatier[2] overlooks the fact that ad-
sorption is specific and consequently draws the conclusion
that adsorption alone cannot account for the observed be-
havior of catalytic agents. "When one assumes a purely
physical cause for the reaction it is impossible to account
for the specific action of catalytic agents and for the sur-
prising differences in the reactions caused by different catalytic
agents. For instance at 300° the vapor of an alcohol, isobutyl
alcohol for instance, is converted exclusively into aldehyde
and hydrogen by copper, and exclusively into isobutylene and
water by alumina, while aldehyde and olefine are formed
simultaneously in presence of uranium oxide, and manganous
oxide acts like copper but more slowly.

"Even if one admits that the fact that copper is a metal
and a conductor of electricity has something to do with the
fundamental difference between its action and that of alumina,
it is still impossible to account for the difference in behavior
of alumina, uranium oxide, and manganous oxide if the
physical phenomena accompanying the adsorption of the gases

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[1] Jour Phys Chem , **17**, 568 (1913).
[2] "Die Katalyse in der organischen Chemie," 240 (1914).

in the pores of the catalytic agent are the sole cause of the catalysis.

"The decomposition of formic acid is another, not less striking, case of the specific action of catalytic agents. Finely divided metals and also zinc oxide decompose the acid exclusively into hydrogen and carbon dioxide while titanium dioxide at the same temperature causes it to decompose into water and carbon dioxide, and other oxides, like thorium dioxide, accelerate both reactions simultaneously, with the possible complication of the formation of formaldehyde and even of methyl alcohol.

"For these reasons one must assume that the pulverulent catalytic agents, such as finely divided metals and oxides, owe their catalytic action to the temporary formation of a compound of the catalytic agent with one of the reacting substances or one of the reaction products. The action of these catalytic agents therefore does not differ essentially from that of catalytic agents which we know to form intermediate compounds that can be isolated In this case of the formic acid, the substance reacting with the catalytic agent is either hydrogen which combines with the metallic catalytic agents, carbon dioxide which is taken up by zinc oxide, or formic acid itself which reacts with the oxides giving formates that decompose in different ways The formic acid molecule is not especially stable and tends to decompose either into $CO + H_2O$ or into $CO_2 + H_2$. Which of these two reactions takes place depends on the specific affinity of the catalytic agent and the consequent formation of a definite intermediate compound.

"We have previously seen that when the fatty acids are decomposed catalytically by oxides, the ketone is formed through the break-down of a salt formed as an intermediate product. These salts can be detected in several cases if one works at a temperature below that necessary for catalysis At higher temperatures these salts cannot be detected because they decompose as fast as formed. With some oxides, such as thorium dioxide and titanium dioxide, the inter-

mediate formation of a salt cannot be detected, presumably because the temperature at which it should form is not lower than the decomposition temperature. The analogy is so complete that one must assume that the reaction takes place in the same way with all of the oxides.

"This conception of the way in which catalysis occurs is supported by the experimental confirmation of the predictions which one can make. If the metallic catalytic agents, nickel, copper, etc., tend to react with hydrogen, forming intermediate products analogous to the hydrides, these metals must also be able to remove hydrogen from substances which can give off hydrogen. In other words, these metals should act as dehydrogenizing catalytic agents. It was this line of thought which caused Sabatier and Senderens to try these metals as catalyzers for the decomposition of alcohols into hydrogen and aldehydes or ketones. It was found that nickel was less suitable than copper for this purpose because of its tendency to form with carbon monoxide an intermediate compound which was instable at the temperature of the reaction and which gave rise to a secondary decomposition of the aldehydes and ketones.

"Sabatier and Mailhe have also accounted for the exclusively dehydrating action of the oxides of aluminum, thorium, and tungsten, on alcohols by ascribing to them the same part which sulphuric acid plays in the Williamson process. Thorium dioxide first forms an alkyl thorate which is decomposed by heat into olefine and regenerated thorium dioxide. If this is really so, this thorate being a kind of ester, should react chemically with substances brought in contact with it. This assumption has been confirmed experimentally in great detail by Sabatier and Mailhe.[1] In contact with thorium dioxide alcohol vapor reacts directly with hydrogen sulphide, ammonia, phenols, and fatty acids, forming mercaptans, amines, phenol, ethers, and esters.

"Ostwald criticized the assumption of intermediate products because it does not rest on a sufficiently accurate know-

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[1] Comptes rendus, 150, 823 (1910).

ledge of the reactions, and also because it is not proved that the direct reaction takes place less rapidly than the total of the hypothetical intermediate reactions. He further expresses the opinion that all theories are worthless so long as no accurate measurements exist.

"The theory of intermediate reactions in catalysis is open admittedly to the criticism of requiring here and there the assumption of hypothetical compounds; but it is impossible to give any other general explanation of the catalytic phenomena."

Sabatier's position is essentially a defensive one. His real claim is not that his theory is good in itself, but that no other makes any pretense of accounting for the facts. That is certainly not true nowadays. All of Sabat er's arguments can be rewritten without trouble in terms of selective adsorption, which has the advantages that it can be tested experimentally and that it accounts for the action of titanium oxide on alcohols, a point which Sabatier's theory does not pretend to explain. On the other hand it must be admitted that it has not been shown that the relative adsorptions are always what they should be to explain the reactions. Until that has been shown we are in the position of substituting hypothetical adsorptions for hypothetical intermediate products. Personally, I think that it is an improvement to do so; but I recognize that this is a point on which opinions may differ temporarily. The poisoning of catalytic.agents is very difficult to account for if we assume the existence of intermediate compounds, whereas it becomes quite simple if we consider that the adsorption may be decreased enormously. Of course, it is still to be proved that all substances which poison catalytic agents do cut down the adsorption of the essential reacting substances or reaction product, but that again is a matter which can easily be tested experimentally.

The general conclusions to be drawn from this paper are:

1. Only those substances which are adsorbed by a solid are catalyzed by it.

2. While the catalytic action of solids may be solely

Wilder D. Bancroft

the result of the increased surface concentration in some cases, this is not always the only factor.

3. A solid catalytic agent may be considered as equivalent to a solvent and may therefore displace the equilibrium.

4. As a result of selective adsorption we may get different reaction products with different catalytic agents.

5. A catalytic agent tends to produce the system which it adsorbs the most strongly.

Cornell University

NEW BOOKS

Science and Learning in France. *Edited by John H. Wigmore. 24 × 17 cm; pp. xxxviii + 454. Chicago: The Society for American Fellowship in French Universities. 1917. Price: $1.60.*—Among the requirements for an advanced degree in France was the one that the candidate must have the preceding French degree. An American degree from any American college did not suffice. This requirement made it impossible for an American student to obtain an advanced degree in France in any reasonable time, and this is one reason why American students went to Germany where no such barrier existed. It is also easy to see that an American professor who had received part of his training in Germany would naturally tend to send his students to Germany for further study. The French universities have now removed the obstacle which they themselves had created. There is now every reason why American graduate students should take advantage of the opportunities which hitherto were practically closed to them—assuming that they are going abroad to pursue their researches.

In the preface the editor says: "Our purpose in this volume is, primarily, to put before the American public the contributions of France in all fields of scientific knowledge, and to show her status in the forefront of the world's progress; and, in addition, to furnish to American university students all information bearing on graduate work in France.

"Each chapter sets forth briefly, for a particular field:

1. The record of French scholarship during the past century; the notable achievements; the eminent leaders; the special lines of development; in general, the share of France in the world's progress;

2. The course of instruction given, now or recently, at the universities of France, particularly at the University of Paris; the names of the most important scholars, with mention of their principal contributions and of the special fields of research over which they preside;

3. The facilities available for study and research, including the libraries, laboratories, archives, and museums, the auxiliary institutes, special schools, and learned societies and committees.

"There is also·

An introduction, describing the general intellectual spirit of France and Paris, and the interest and attractions that capital and country offer to the foreign scholar; and

An Appendix, describing the organization of French universities, the standards of preparation expected of the student, the system of degrees, the customs as to residence and attendance, the regulations as to fees and the like; and other facts useful to the visiting student.

"The book has been made possible by the liberality of the Society for American Fellowships in French Universities, which has borne all the expense of publication.

"The ultimate and cardinal mission of the book will be an act of homage to French science. Let the scholars of France know that their American colleagues are eager to pay this just tribute! The great place of France in the world of knowledge—the place that it always has held and always will hold—can never be forgotten by their debtors on this side of the ocean.

"The men who wrote this book are qualified to speak on their subjects; a glance at their names will show that their word is decisive. They represent American scholarship. They have spoken frankly, sincerely, and judicially, without reserve or exaggeration.

"Their message goes out to the American people. May it convey some fresh light to our fellow-countrymen, and help to fix in their conviction the true status of French learning in the world!

"This book was planned and begun towards the end of the year 1915; and in presenting it now, when the bonds of mutual esteem and gratitude between France and America have been drawn even more closely, the authors belive that they are not only pointing the youth of our country to splendid sources of knowledge and wisdom, but are also serving, in the measure of their ability, to strengthen and confirm that comradeship of scholars which symbolizes the enduring friendship of the two nations."

The volume opens with an article on "The Mind of France," by Ex-President Eliot.

"In the eighteenth and nineteenth centuries, France produced a large number of great masters in all fields of thought—in literature, science, and the arts. She thus kept abreast of all intellectual progress in Europe, and often led the way.

"These great men were usually skilful teachers as well as creators and discoverers; so that they had worthy disciples—groups of younger scholars who spread abroad the masters' ideas, and prolonged their influence by adding the needed interpretations and modifications. In many fields, the works of these French leaders set standards not only for France, but for the world.

"Their intellectual work possessed, as a rule, certain qualities which characterize the French mind, such as broad sympathy, constructive imagination, and a tendency to prefer the concrete or realistic to the abstract, and fact to speculation. These intellectual characteristics of the French have proved to be extraordinarily permanent, abiding generation after generation, and surviving immense political and social changes. The French scholar is apt to be an open-minded man, receptive toward new ideas, and an ardent lover of truth, fluent and progressive. The French scientists have rarely been extreme specialists, narrow in their interests and their chosen objects. They have recognized that no science can be pursued successfully in isolation; its affiliations and adjuncts must also be studied. They have not been subdued by the elaborate sorting and compiling machinery of modern scholarship.

"The French people under all their forms of government—monarchical, imperial, or republican—have always shown cordial appreciation of intellectual achievements, and particularly of scientific investigation in philology, history, physical science, biology, sociology, and law. They place high among their national heroes their great scholars, writers, artists, and scientists. This popular appreciation has given vitality and enduring national influence to French scholarship in a great variety of fields.

"All French masters in science and literature have had the advantage, in expounding and communicating the fruits of their labors, of expressing themselves in the French language, which lends itself to elegance and clearness, and to nice discrimination and perfect accuracy in statement. It is well-nigh impossi-

ble for teacher or expounder to be clumsy, obscure, or disorderly in the French language. Indeed, many of the most profound French philosophers and investigators have also exhibited a high degree of literary skill. A French style may be exaggerated, redundant, or diffuse, but it never fails to be clear. The French language, therefore, has been of great advantage to the French masters of thought, and through them to all the students who follow them—native or foreign.

"To an unexampled degree the spirit of liberty has animated all the French leaders and schools of thought for two centuries. For them intellectual inquiry has been free. This is true not only in the field of social and political ideas and the philosophy of government, but also in the institutions intended to promote the development of science, literature, and art. The French Academies of Science and Letters all illustrate it, and so do the noble professional traditions in French Courts of Justice and the French Bar, both the Courts and the Bar having set high examples of courage, independence, and bold insistance on judicial and professional privileges. Science, letters, and art in France have always shared, and often enkindled, the people's love of freedom and their passionate advocacy of democracy.

"American students, thinking to take advanced studies in Europe, have often in times past supposed the French to be an inconstant, pleasure-loving, materialistic people. They have now learned through the Great War the French are an heroic people, constant to great political and social ideals, a people intelligent, fervid, dutiful, and devoted to family, home, and country. They have also come to see that the peculiar national spirit of France is one of the great bulwarks and resources of civilization, which ought to be not only preserved, but reinforced."

The subjects about which the book gives information are listed alphabetically as: anthropology, archaeology, astronomy; botany and agriculture; chemistry; criminology; education; engineering; geography, geology; history; law; mathematics; medicine; classical philology; romance philology; oriental philology; Semitic philology; English philology; philosophy; physics; political science; psychology; religion; sociology; zoölogy. The information in regard to chemistry covers the professors in Paris, Besançon, Bordeaux, Caen, Clermont, Dijon, Grenoble, Lille, Lyon, Marseilles, Montpellier, Nancy, Poitiers, Rennes, and Toulouse.

The dedication is worth placing on record here.

"To the scholars of France, worthy custodians of their country's intellectual greatness, this volume, prepared in a time when France has reached the heights of moral greatness, is offered with heartfelt admiration and sympathy in the name of the scholars of America." *Wilder D. Bancroft*

The Life of Robert Hare. *By Edgar Fahs Smith. 25 × 17 cm; pp. x + 508. Philadelphia: J. B. Lippincott & Co., 1917. Price: $5.00, net.*—In the preface the author says: "This volume contains the life story of one of the greatest scientists of our country. His chief delight was in chemical pursuits, although his attachment to physics was also great. He was a true pioneer in these divisions of science. His experimental contributions were of a very high order in their day. They commanded respect and admiration then and continue

to do so in the present because they represent the beginnings of so much that has come to be of prime importance. When, in the future, the contributions of America's earliest representatives in the many fields of science are scanned more closely, an abundance of noteworthy material will be discovered and our country, although young, will be found to have given her share to the sum total of human knowledge."

Robert Hare was born in Philadelphia in 1781; he was appointed professor of chemistry in the University of Pennsylvania in 1818; he resigned this chair in 1847; and he died in 1858. Hare made a surprising number of striking inventions. When only twenty-one he invented the oxyhydrogen blowpipe thus increasing the available temperature range very considerably. As the author says, p. 5: "This discovery gave the indubitable evidence of a highly philosophical mind in its author, for then the notions of the real nature of combustion were extremely vague, and that Hare should have had the acumen to conceive that a stream of oxygen and hydrogen burning together would produce so intense a heat was extraordinary. It was a splendid triumph for him. And when it is realized that from this discovery sprang, among others, the lime light or Drummond light, universal gratitude is due to this youthful adventurer in the field of pure and applied science. The intense heat of the oxyhydrogen blowpipe enabled Hare to fuse platinum, so that some years after the discovery had attained a higher degree of perfection, a student of Hare, familiar with the compound blowpipe, set forth to found in this country an industry in the working of platinum. Indeed, Bishop's Platinum Works of to-day is the modern development of Joachim Bishop's pioneer effort. From the beginning, its several steps were crowned with success "

In 1818 Hare invented the calorimotor, a voltaic battery with the cells mostly in parallel instead of in multiple. When short-circuited with a wire having a relatively low resistance, this battery of course gave a very large current heating the wire to incandescence or even fusing it. The calorimotor is equivalent to a two- or three-cell battery with enormously large plates.

A couple of years later Hare invented an instrument which he called the deflagrator. It is not clear from the text whether the deflagrator is an improved calorimotor or whether it is an improved voltaic battery with the cells in series. The two important features about it were that the plates were put very close together in coils so that the internal resistance was made low; and that the plates could be immersed in the liquid or raised out of it simultaneously so that a very high current was obtained before the cells polarized partially. When a piece of charcoal about two inches long, p. 90, was used to complete the circuit "the submersion of the coils caused the most vivid ignition in the coal. It was instantaneously and entirely on fire. A piece of platina of about a quarter of an inch diameter in connexion with one pole, was instantly fused at the end on being brought in contact with some mercury communicating with the other. When two cylinders of charcoal having hemispherical termination were fitted into the brass cylinders and brought nearly into contact, a most vivid ignition took place, and continued after they were removed about a half or three-quarters of an inch apart, the interval rivalling the sun in brilliancy."

Hare was never very clear as to the theory of these instruments, p. 91. "As points are pre-eminently capable of carrying off (without being injured) a

current of the electrical fluid, and very ill qualified to conduct caloric; while by facilitating radiation, charcoal favors the separation of caloric from the electricity which does not radiate; this result seems consistent with my hypothesis, that the fluids, as extricated by Volta's pile, is a *compound of caloric and electricity* but not with the other hypothesis which supposes it to be *electricity alone*. The finest needle is competent to discharge the product of the most powerful [friction] machines without detriment, if received gradually as generated by them. Platina points, as small as those which were melted like wax in my experiments, are used as tips to lighting rods without injury, unless in sudden discharges, produced under peculiarities. * * * * According to my theory, caloric is not separated from the electricity until circumstances very much favor a disunion, as on the passage of the compound fluid through charcoal, the air, or a vacuum." Instead of criticizing this conception severely, one should remember that all this happened nearly twenty years before the formulation of the law of conservation of energy, and while the whole question of heat was a very puzzling one.

In 1839 Hare constructed an electric furnace with which one could work in any atmosphere or in a vacuum. With this he prepared calcium carbide, phosphorus, graphite, and calcium. In regard to this, the author says, p. 498: "How is all this to be regarded? Is it to be designated as primitive? Yes, it is that; but does it not stamp its originator as a true pioneer in a field which today is cultivated most assiduously and extensively with astonishing outcome? Probably none of those who have developed the field of practical electro-chemistry have ever read a description of Hare's furnace; but it was built by him and with its assistance he obtained products which called forth little enthusiasm, then dropped from view, and which are now of common occurrence."

As minor things Hare showed that the luminosity of the hydrogen flame can be increased by the addition of turpentine, p. 79; he constructed eudiometers for gas analysis, p. 498; he invented an improved vent-peg for beer casks, p. 20; he used platinized sponge to synthesize ammonia by the action of hydrogen on nitric oxide, p. 201; and he used a mercury cathode in preparing barium, strontium, and calcium amalgams. In regard to this, the author says, p. 311. "In this process Hare uses mercury as cathode in an aqueous salt solution. It is probable that this was the first time that the metal had been so employed, and would it not then have to be regarded as the forerunner of its use in making caustic soda from an aqueous sodium chloride solution? Was it not also the forerunner of the employment of mercury as cathode in electro-analysis? It will be recalled that in 1841 Wolcott Gibbs acted as student assistant in Hare's laboratory, and it does seem quite probable that the things which had so deeply interested Hare and occupied so much of his thought would be the subject of discussion with his assistants, so that in later years when Wolcott Gibbs was enriching the domain of analytical chemistry with his contributions, he may have recalled his old Philadelphia experiences and used mercury placed in a small beaker as cathode in the electrolysis of copper and nickel sulphates; and later Drowne (his former pupil), used it in the electrolysis of iron phosphates, while thousands of determinations and separations of metals have since been expeditiously and accurately effected in this way. Surely it is not too much to claim for Hare the pioneer work in the use of mercury as cathode in industrial and analytical operations."

In the period after resigning the chair of chemistry, Hare interested himself in meteorological problems; he wrote a novel; and he became a spiritualist. It seems probable that he had actually burned out. He was entitled to rest for he had done much. As the author says in the preface: "Robert Hare, an American chemist, will surely live in the memory of all who become acquainted with him through his epoch-making contributions to that science which is so closely interwoven with the welfare, comfort, and happiness of mankind."

Wilder D. Bancroft

A German-English Dictionary for Chemists. *By Austin M. Patterson. 18 × 13 cm; pp. xvi + 316. New York: John Wiley & Sons, 1917. Price: $2.00.* —In the preface the author says: "As the title is meant to imply, this book is not solely a dictionary of chemical terms. It includes words from related fields of science and, what is perhaps a novelty in a technical dictionary, a *general* vocabulary. More attention has also been paid to abbreviations, prefixes, and suffixes than in the average work of its kind. For historical reasons a number of old terms are defined; where these might be confused with modern meanings they are distinguished by the label *"Old Chem."* or in some other way. It should be remembered, too, that some terms which have been replaced in chemistry are still in use in pharmacy or industry. If some of the chemical industries do not seem to be represented in due proportion, this must be ascribed to the fact that glossaries of them are not available and that war conditions have made it extremely difficult to secure German books. It is hoped that these departments may be added to in a later edition."

The book is an admirable one and will be of great value to the student of chemistry. In fact he really cannot do without it.

Wilder D. Bancroft

A Memoir on British Resources of Sands Suitable for Glass-Making. *By P. G. H. Boswell. 21 × 14 cm; pp. 92. London: Longmans, Green & Co., 1916. Price: 50 cts.*—"Minute study of the sands employed in the manufacture of glass has revealed the fact that the very exceptional qualities displayed by the best of them are not due merely to chemical composition but are the outcome of their exact mineralogical nature, and even of the size and shape of their constituent grains." This rather startling statement is true only so far as the economic production of glass is concerned. When the grains of sand are all of the same size and the same structure, they will react with alkali at practically the same rate and it is not necessary to continue heating the mass an additional length of time so as to form silicates out of the larger grains. There are a good many interesting facts in this pamphlet, but the author too often neglects to give any theoretical explanations for his dogmatic statements. It is not clear whether he does not know the reasons himself or whether he thinks that technical men do not care for reasons, but the pamphlet does fall short of what it should have been.

The subject is presented under the headings: introduction; the nature of sands; methods of study of sands; glass manufacture; the requirements of a good glass sand; sands suitable for glass-making; special treatment of sands and rocks; economic considerations.

Wilder D. Bancroft

THE STABILITY OF EMULSIONS IN THE CONSTRICTED TUBE AND MARBLE DEVICE FOR ANAEROBIOSIS[1]

BY IVAN C. HALL

In comparing the marble seal in the constricted tube[2] with a seal of hydrocarbon oil in the cultivation of obligative anaerobic bacteria it was repeatedly observed that growth in the tube sealed by the latter method and especially when inoculated with minute quantities of culture, was considerably less rapid and gas formation in glucose broth less abundant. That inhibition is not due to antiseptic properties of the oil was easily shown by as early growth as usual in media containing an excess of oil but sealed by means of the marble in the broth.

In connection with this fact, and more particularly some experiments as yet unpublished on methylene blue as a criterion of anaerobiosis, I was led to the observation that if the marble is placed in the oil, and the tube heated in a bath of boiling water, on cooling, the oil below the marble becomes markedly opaque, due, as shown by further study, to emulsification of water in the oil. The oil open to the air, however, remains quite clear, or, if an emulsion is formed at all, as it can be by rapid cooling, it persists for a short time only. The emulsion below the marble, on the contrary, is moderately stable, and consists of microscopic drops of water in oil. The excess of water in the base of the tube remains throughout perfectly clear. The development or stability of such an emulsion does not depend upon the presence of any of the usual constituents of culture media, being obtained with distilled water and hydrocarbon oil. Two immiscible liquids are, of course, necessary; oil heated alone in a

clean *dry* tube remains clear on cooling. In experiments to test the effect of hydrochloric acid, sodium hydroxide, and sodium chloride solution, instead of distilled water, no difference in the formation of emulsions could be detected. Solutions ranging from normality to hundredth normality showed no difference in the *stability* of the formed emulsions at ice chest temperature (about 6° C) during the first 48 hours. After 96 hours the emulsions formed over N/1 and N/5 NaCl were clearing, at 120 hours also that over N/1 NaOH; all the rest were subsiding slightly. The differences were not marked and seemed to justify the conclusion that the effect of these substances, i. e., acids, bases and salts, is rather a minor one. Since hydrocarbon oil is a non-saponifiable compound even vigorous shaking with strong alkali fails to produce a stable emulsion.

A simple explanation of the *formation* of the emulsion suffices. The solubility of water in oil, though slight at low temperature, is increased as the temperature is raised. When the temperature is reduced, the water precipitates in the oil; on raising the temperature again the emulsion disappears by redissolving. As to why emulsions form so much more readily and persist so much longer below the marble seal constitutes the point of interest in this paper.

Emulsions may be prepared by this method not only with water and hydrocarbon oil but also with water and any one of the following, to wit: gasolene, heptane, chloroform, xylol, ether, benzol, kerosene, carbon bisulphide, commercial lubricating oil, olive oil, and aniline. In every case water forms the internal phase; this is true even with immiscible liquids heavier than water, e. g., chloroform and carbon bisulphide, and also with liquids more volatile than water such as heptane, chloroform, ether, benzol and carbon bisulphide. Some special cases must be considered. For example, olive oil and "zerolene" (a commercial automobile cylinder oil) emulsify very slowly though finally very heavily; this may be attributed to their high viscosity which tends to prevent the coalescence of the precipitated water. A tube of 15 cc of zerolene with 5 cc of distilled water in the base and sealed

with a marble in the oil was still heavily emulsified below the marble after ten months at room temperature. Even without the marble seal there is a tendency to permanent emulsification in the oil near the oil-water surface in this instance. The emulsification of water in ether is very slight, which may be explained partly as due to the impossibility of raising the temperature above the boiling point of ether in the open air. It is to be noted in several cases, however, e. g., carbon bisulphide, benzol and chloroform, that the boiling point of water is not nearly reached, yet the solubility of water in these compounds is sufficiently increased at the lower temperature to produce a marked turbidity on cooling. In all but benzol, xylol, and aniline, water forms the internal phase only; with benzol and xylol water forms also the external phase of an emulsion, and with aniline the emulsion of the oil in the water is more prominent than that of water in the oil though both occur—the latter principally in the depths. Aniline constitutes a very special case; it is lighter than water above 70° and heavier than water below 65° C. Heated in a bath of boiling water, and cooled, the mixed liquids form two thick emulsions, first, of oil in water, then of water in oil. And the position of large oil drops in the water with respect to the air-liquid surface determines whether an emulsion of water shall or shall not form in them, those in the depth emulsifying first and most distinctly.

In all cases tried, emulsions of water in water-immiscible liquids form more quickly and with less cooling under the marble seal in the constricted tube. And when emulsions are formed without the seal, as they can be in most cases by especially rapid cooling, as, for example, in ice water, the stability has been found to be slight as compared with similar emulsions protected by the marble seal.

No doubt many valuable points might be gleaned as to the necessary temperature of the initial heating, the degree and rapidity of cooling, et cetera, but it is necessary to refrain from discussing these interesting quantitative questions for the present. We may pause to mention, however, that the

stability of emulsions of water in zerolene and olive oil under the marble seal is a matter of months and of water in carbon bisulphide, hydrocarbon oil, kerosene, and xylol of days as Table I shows:

TABLE I

Stability of emulsions of water in various immiscible liquids

Substances	Maximum temperature of heating	Stability at ice chest temperature	
		Without marble	With marble seal
Zerolene	98.5° C	Less than 3 days	More than 240 days
Olive oil	98.5° C	Less than 1 day	More than 61 days
Carbon bi-sulphide	52 ° C	Less than 1 day	More than 21 days
Hydrocarbon oil	98.5° C	Less than 2 days	More than 7 days
Kerosene	98.5° C	Less than 1 day	More than 2 days
Xylol	98.5° C	Less than 1 day	More than 1 day

The stability of emulsions of water in benzol, ether, chloroform, heptane, gasolene, and aniline, however, is a matter of hours in the constricted tube with marble seal as compared to similar tubes without such seal, but always greater in the former. The possibility of producing emulsions in other immiscible combinations than those involving water is suggested. I have experimented mostly with emulsions of water in hydrocarbon oil (Langley and Michaels, San Francisco).

For the successful preparation of emulsions of water in oil various mechanical devices are suitable. The biconvex disc, a circular cover slip in a constricted tube, or a cover slip in a plain test tube, as previously described for cultivation of anaerobic bacteria, all give results comparable to those obtained by using the marble. A five cent piece or a copper disc (cleaned by dropping while red hot into methyl alcohol) serve equally as well as the glass or porcelain seal. It is only necessary that there be a few drops of water in the base of the tube with the oil overlying and some of the oil below the seal. The system is heated a few moments in a bath of

boiling water, the liquids above and below the seal then being clear. On cooling, the emulsion forms in the oil below the seal.

The Smith fermentation tube, which, barring its objectionable high initial cost, difficult cleaning, handling and heavy breakage, most nearly approaches the constricted tube in availability for anaerobic cultures, serves admirably for demonstrating the persistence of water-oil emulsions. If the water reaches above the bend in the tube so as to separate the oil in the closed arm completely from that in the open arm it is found that the former remains turbid for an indefinite period of months while the latter fails to emulsify except by rapid cooling and such emulsions are very instable. If the water fails to reach the bend in the tube, the emulsion formed in the oil of the closed arm disappears slowly by diffusion into the open arm.

It seemed at first that the formation and especially the persistence of these emulsions was definitely dependent upon the comparative absence of air from the oil and the term "anaerobic emulsions" was tentatively used; my interest as a bacteriologist seemed therefore to be justified, from the standpoint of cultivation of anaerobes, in this physical problem, especially as I had abundant evidence of the inferiority of oil as a means of securing vigorous anaerobic growth. It seemed, indeed, as if the observation that oil layered upon culture broth for anaerobes fails to remain emulsified might be used to explain this inferiority providing it could be shown that the persistence of the emulsion in the constricted tube was dependent upon a superior exclusion of air due to the marble.

But further study shows that temperature and evaporation play more important rôles in determining the instability of the emulsion. We know that as the temperature is raised the solubility of the water in the oil increases. The concentration of water in the deep layers of oil is greater than at the air surface because of constant evaporation of water into the air from the surface of the oil. Therefore when cooling

starts, emulsification begins to be visible near the oil-water surface. Similarly on heating a water-oil emulsion formed by rapid cooling in a tube without the marble seal the turbidity disappears first at the air-oil surface. The particles of water may be seen to diffuse rapidly upward; when they reach the air-oil surface they undoubtedly evaporate and their places are filled by others, resulting shortly in a disappearance of the emulsion. But if a barrier to diffusion, such as the just-described mechanical seal, be interposed, evaporation is prevented and the emulsion is relatively stable.

If evaporation is the main factor in determining the instability of the emulsion, it should be operative even in the presence of air. This is, indeed, the case; emulsions of water in hydrocarbon oil formed in a long tube (1 cm × 60 cm) open to the air without a seal are moderately stable, whereas in a similar tube only 10 to 12 cm long special precautions for rapid cooling have to be followed to secure an emulsion at all and the stability is short lived. In the Smith fermentation tube also, if a bubble of air be admitted to the closed arm of a tube containing oil with water in the base reaching above the turn in the tube the emulsion formed by heating and cooling is as stable as without the air bubble, while the oil in the open arm freely exposed to evaporation forms only a transient emulsion with the water in the base.

These facts indicate that the presence or absence of an air surface above the emulsion is immaterial and the real factor in the lack of stability in these water-oil emulsions is evaporation.

Further evidence of the importance of evaporation rather than the presence of air was found in some pairs of tubes containing water-oil emulsions in which one tube was sealed while boiling in a water bath and under a vacuum of over 71 cm mercury, the other sealed cold in the open air. Both tubes having finally been boiled and cooled with resultant formation of emulsions, it was regularly observed that the emulsion in the tube having a lowered air pressure was less stable. This is exactly contrary to what would be expected

if the stability depended upon the absence of air and the tendency of emulsions to disappear in such tubes sealed under partial vacuum can be explained best as due to evaporation of the water droplets from the oil surface, as shown by the condensed droplets visible along the sides of the tubes.

Discussion

Interest in these observations lies especially in their bearing upon the theory of emulsification. There is nothing new in the formation of emulsions by cooling two relatively immiscible liquids whose mutual solubility has been increased by heating, Ostwald[1] having noted this method as available in determining the relation between solubility and temperature. But no record of the comparative permanence of emulsions formed in this manner by two immiscible liquids, and especially without the known presence of a so-called emulsifying agent, has come to my attention. The closest suggestion is that in which Pickering[2] said, "although one of these semi-solid emulsions (of kerosene and soap solution) when kept in a closed vessel will only gradually de-emulsify in the course of months, yet, when exposed to dry air, it will do so in a short time; the edges of the lump assume the appearance of a transparent, slightly blue jelly, and the whole liquefies in the course of some hours. No such change occurs in moist air." Bancroft[3] commenting, confidently ascribed the instability of Pickering's emulsions in dry air to evaporation of the water with resultant coagulation of film and release of the kerosene drops.

In my experiments evaporation is one of the fundamental causes of de-emulsification, but the situation is different because in Pickering's petroleum jelly it is the external or dispersing phase which evaporates while in my experiments it is the diffusion and evaporation of the internal or dispersed phase which destroys the emulsion.

[1] Ostwald: "Manual of Physico-Chemical Measurements," p. 175 (1894).
[2] Pickering: Jour. Chem. Soc , **91**, 2001 (1907).
[3] Bancroft: Jour. Phys. Chem., **16**, 475 (1912).

Determination of Phases

It is significant that in these emulsions water forms the internal or dispersed phase with oil as the external or dispersing phase. Bancroft[1] cited Ostwald's[2] use of the principle that wetted surfaces tend to destroy the dispersity of that phase and conserve the dispersity of the opposite phase, in determining the distribution of two immiscible liquids in an emulsion as follows: "If one dips a piece of filter paper into an oil-water emulsion in which the oil is present as drops, the filter paper becomes wetted with water and the oil drops off. If the filter paper is dipped into an emulsion in which water is present as drops we get an oiled paper from which the water runs off." Newman[3] has mentioned three methods of determining the phases of an emulsion, namely (a) inspection, (b) the indicator method of Robertson[4] and (c) the drop method of Briggs.

In my experiments inspection sufficed in every case to show the distribution of the phases because of an unemulsified excess of each component and the result of inspection was confirmed by each of the other methods in the case of water-hydrocarbon oil emulsions. Of Ostwald's and Briggs' methods the latter gives the more clear-cut result. Robertson's method was easily applied, using not only Sudan III but also such oil-soluble dyes as Scharlach Roth (Grübler) and Dimethyl-amido-azo benzene (Merck). Newman has also mentioned the applicability of iodine and methyl orange in Robertson's method, the first being oil-soluble, water-insoluble, and the last, vice versa.

' I made the reverse test also, using the water-soluble, oil-insoluble dye, Nilblau (Grübler); the dye fails to diffuse through the emulsion, but the test is not completely satisfactory, owing to the fact that the water adheres to the glass all along the inside of the tube even when the tube has been

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[1] Bancroft: Jour. Phys. Chem., **16**, 177 (1912).

[2] Ostwald: Zeit. Colloidchemie, **6**, 103 (1910).

[3] Newman: Jour. Phys. Chem., **18**, 34 (1914).

[4] Robertson: "The Proteins," Univ. of Calif. Pub. in Physiology, **3,** 115 (1909).

first rinsed in oil, and this film of water becomes stained. Incidentally, this explains a failure to find any difference in stability of emulsions in an oil-wet tube and in a water-wet tube for the oil-wet tube becomes water-wet very soon on heating.

A simple method of determining the phases of not too opaque emulsions was found as follows: A drop of one of the liquids is placed in the emulsion near but not touching the glass. If it is dispersoid it is clearly delimited and moves up or down through the emulsion; if it be the dispersing medium it diffuses quickly into its surroundings making a slightly less opaque area. In the case of water-hydrocarbon oil emulsions, water sinks as a clear drop; oil rises and diffuses. If a water drop is touched to the glass it quickly breaks and runs down the water film into the excess of water below; it was this, in fact, which first drew my attention to the water film on the glass. In this case the wetted surface of the glass apparently does not destroy the dispersity of that phase (water) and conserve the dispersity of the opposite phase (oil). In the constricted tube and marble device this film serves to isolate completely the emulsified oil below the seal from the unemulsified oil above; it therefore insures the retention by the oil of the maximum number of precipitated water globules at any given temperature. The complete isolation of the emulsified oil from the unemulsified oil is to be observed best during the period of cooling, when large agglomerated droplets of precipitated water may frequently be seen to find their way from above to below the marble, there forming an easily visible layer of water over the oil, continuous with the film on the glass and the excess of water in the base. This observation leads one to infer that not all of the water which dissolves in the oil at an increased temperature necessarily becomes emulsified on precipitation.

In the Smith fermentation tube also the mass of emulsified oil is kept saturated with water by the act of its complete boundary of water or water saturated atmosphere which effectually prevents evaporation of the water particles.

Emulsifying Agent

It should be noted particularly that fairly stable emul-
sions may now be prepared with certain liquids which probably
do not react mutually to form an emulsifying agent as in the
case of weak alkali and olive oil. Lewis[1] claimed to have pre-
pared stable emulsions of as much as 2 percent mineral oil
in water by 48 hours' vigorous shaking but Bancroft[2] criticized
Lewis in his assumption that a two-component emulsion is a
thermodynamically stable system, pointed out that "there is
nothing in the discussion to show why there should be a 2
percent limit," reached the conclusion that "all the evidence
that we have is to the effect that no two-component colloidal
suspension is stable," and inferred that the same probably
applies to emulsions.

Ellis[3] also studied two-component emulsions containing
one part of oil in 10,000 of water, which were not very stable.
Moreover, in Ellis' work the possibility of oleic acid as an
emulsifying agent was not wholly ruled out though it was
determined as less than 0.03 percent. Summarizing the work
of the various investigators, Bancroft in 1912 concluded that
"to obtain a more stable and concentrated emulsion, a third
substance must be added as an emulsifying agent. When
water is the dispersing phase the emulsifying agent should
lower the surface tension of the water (Quincke, Donnan) and
should be viscous (Quincke, Hillyer)."

In the case of emulsions formed by heating and cooling
it is obvious that the quantity of water which will become
emulsified in the oil is limited primarily by the solubility of
the water in the oil at the maximum temperature to which the
system is heated before cooling. If the explanation given
of the stability of these emulsions through the limitation of
evaporation is correct, it is difficult to see that an emulsifying
agent is necessary. Viscosity, however, appears to be an im-
portant factor in determining the stability of such emulsions.

[1] Lewis: Zeit. Kolloidchemie, **4,** 211 (1909).

[2] Bancroft: Jour. Phys. Chem., 16, 177 (1912).

[3] Ellis: Zeit. phys. Chem., **78,** 321 (1911).

Pickering[1] has suggested that surface tension and viscosity are less important factors in some cases than is generally supposed, in fact, certain emulsions can be stabilized by using precipitates or suspensions as emulsifying agents which have but slight effect upon the surface tension of water. He mentions that "dilute soap solutions are not very viscous and yet their power of forming an emulsion may even be destroyed by increasing the concentration and thereby the viscosity above a certain point." While these factors may often facilitate emulsification "the only or rather the chief cause of emulsification seems to be the presence in the liquid medium of small insoluble particles which form a film round the drops of oil and keep these from coalescing. In order that such particles should have the power of forming an emulsion, they must have only a very slight tendency to agglomerate, they must be more readily wetted by the water than by the oil, and they must not be crystalline." This view, essentially similar, as Pickering says, to that formed independently by Ramsden,[2] is not identical but relates closely to Höber's (quoted by Bancroft) that the emulsifying agent should be a hydrophilic colloid in an emulsion where water is the dispersing medium. Fischer and Hooker[3] have recently stated their conviction that the production of stable emulsions is "*always* associated with the discovery of a method whereby the water (or other medium) which is to act as the dispersing agent is *all used* in the formation of a colloid hydration (solvation) compound," and have applied this idea in the explanation of certain pathological and physiological facts. Peculiarly neither Pickering nor Höber recognized the corollary of their explanation, later emphasized by Bancroft, that if water is to be emulsified in oil the emulsifying agent should be a hydrophobic colloid.

Robertson[4] prepared emulsions of water in oil by the

[1] Pickering: Jour. Chem. Soc., **91**, 2001 (1907).

[2] Ramsden: Proc. Royal Soc., **72**, 156 (1903).

[3] Fischer and Hooker: Science, **43**, 488 (1916).

[4] Robertson: "The Proteins," Univ. of Calif. Pub. in Physiology, **3**, 115 (1909).

addition of NaOH to olive oil so that a critical point near
which the transition from oil-water or water-oil took place
could be determined for each concentration of alkali. New-
man[1] criticized Robertson's work to the effect that "what
Robertson thought was an emulsion of water in oil is merely
a cracked emulsion in which the appearance of the oil is changed
by the presence of solid sodium oleate." Newman concluded,
in fact, that no water in oil emulsions are formed with hard
soap, sodium oleate or caustic soda. In the belief that hydro-
philic colloids tend to make water the external phase, while
hydrophobic colloids tend to make water the internal phase,
reagents belonging to the latter group were tried with ben-
zene and water. While certain of these gave unstable emul-
sions success was not achieved by Newman until the trial of,
first, magnesium oleate, and more particularly mixtures of
magnesium and sodium oleate, produced emulsions of water
in benzene stable in some cases for eight weeks. Similar
emulsions were prepared of water in carbon bisulfide.

   These considerations suggest that if there is an emulsi-
fying agent present in our constricted tube experiments it is
soluble in oil but insoluble in water. The glassware used
was specially cleaned in strong boiling lye solution, rinsed in
tap water and finally soaked in chromic acid cleaning fluid
and again thoroughly rinsed and dried. In certain experi-
ments the added precaution was taken of treating the glass
with hot oil and cleaning with ether. These procedures
would seem to eliminate the possibility of chemical impuri-
ties from the glass.

   The certain exclusion of impurities from the oil is more
difficult. It seems, indeed, as if the most stable emulsions
are formed in oils which probably contain impurities, e. g.,
commercial lubricating oil, olive oil and kerosene. Hydro-
carbon oil itself is not a chemically pure substance since it
has a variable boiling point. On the other hand, the carbon
bisulfide used, which gives moderately stable emulsions, was

[1] Newman: Jour. Phys. Chem., **18**, 34 (1914).

Baker's analyzed, sp. gr. 1.27, b. p. 46°–49° with 0.001 percent non-volatile matter only, and no SO_2, SO_3 or H_2S. And the benzol, though giving emulsions of less stability, was Kahlbaum's cryst., free of thiophene; thus while it is impossible to deny absolutely the presence of a chemical emulsifying agent in my experiments the assumption of such an agent seems unnecessary and the writer is very doubtful of its existence under the particular conditions described. The question then arises as to what prevents the coalescence of the water globules with one another and with the water film covering the glass. The answer is, first, viscosity, which tends to limit movement of the particles, and, second, possibly the possession of electrical charges of like sign which by their repellant action prevent contact between water particles and films. As to the latter we can only mention that Lewis[1] appreciated the importance of the interfacial potential in the stability of certain emulsions. In my few experiments having this latter possibility in mind only imperfect evidence was secured of such charges, that is to say, the effect upon the stability of emulsions having acids, bases, or salts in the aqueous portion of the system is not marked.

The writer wishes to acknowledge valuable suggestions and aid given by Mr. L. H. Duschak of the U. S. Bureau of Mines Laboratory at Berkeley in attacking this problem.

Summary

This paper reaffirms the possibility of forming emulsions of two immiscible liquids by first increasing their mutual solubility through heating and then precipitating the one in the other by cooling. More particularly the stability of such emulsions in certain devices used for cultivation of obligative anaerobic bacteria is emphasized and explained as due to the protection from evaporation which these devices afford rather than to the absence of air. Incidentally this explanation fails to indicate the reason for the demonstrated inferiority of hydrocarbon oil as a means of anaerobiosis in

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[1] Lewis: Zeit. Kolloidchemie, **4,** 211 (1909).

comparison with certain mechanical seals. The phases of emulsions have been studied by various known means and a new method of determination of phases is described. Viscosity is mentioned as an important element in determining the stability of emulsions formed in the above manner and the likelihood of electrical charges upon the dispersed particles as the only probable emulsifying agent in these experiments is suggested.

MOLECULAR ATTRACTION. XV.
SPECIFIC HEATS OF THE ELEMENTS AND SOME ENERGY CHANGES

BY J. E. MILLS

Part II

In the previous article values for the specific heat of the elements obtained after a careful collection and critical examination of the data were given, and also certain other tables and data to which references will be made in this article.

Diagram I below gives the atomic specific heats up to 1000° K plotted against the temperature of some of the elements for which the data are most accurate at low tempera-
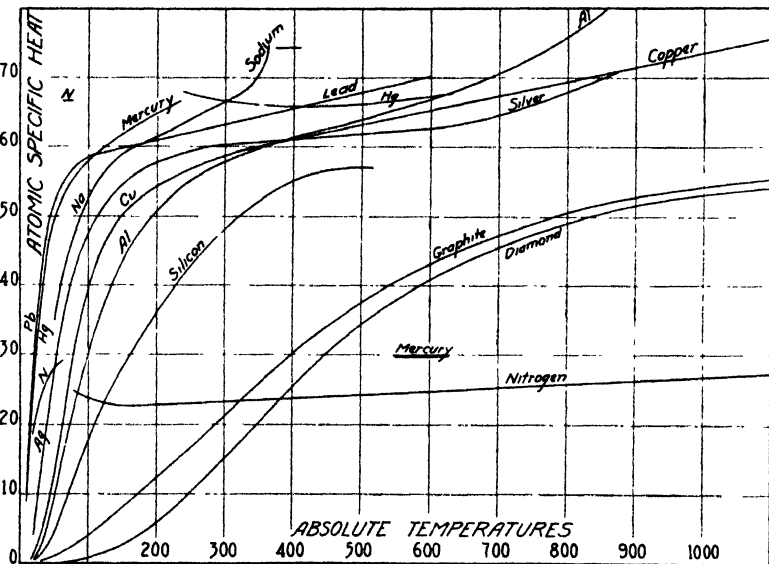
Diagram 1

tures. Some uncertainty attaches to the curve for silver at high temperatures. The unusually rapid rise in the specific heat of aluminum as its melting point is approached only

partly shown in the diagram is not entirely exceptional, but
so rapid a rise is not certainly established. For mercury and
nitrogen the atomic specific heats as solid, liquid, and gas at
constant volume are shown.

The general trend of the curves is apparent to the eye
and need not be discussed. That the curves approach zero
at the absolute zero, seems obvious.

The total heat required to raise a gram atomic weight
of the element to any given temperature is represented by
the area bounded by the curve, the ordinate at the tempera-
ture in question, and the abscissa. That only a very small
error can be introduced into the total heat by extrapolating
the curves to the absolute zero is apparent.

If the law of Dulong and Petit were exactly true as orig-
inally proposed all of the curves should be represented by a
straight line parallel to the temperature axis at 6.25. That
boron, carbon, and silicon were exceptions was soon recog-
nized. It was then supposed that at high temperatures
the curves for these elements would approach the value 6.25.
This is indeed probably true, but with rise in temperature
the atomic heat of all of the other elements also continues
to increase. The curves shown on the diagram are quite
representative, and at no temperature do the atomic specific
heat curves coincide, or even nearly so (except at the abso-
lute zero). If the monatomic metallic elements alone are con-
sidered there is no real coincidence of the atomic heat curves
at any temperature. *The lines for most such monatomic
metallic elements do roughly converge at about room tempera-
ture.* At 0° C, for instance, the average value for the atomic
specific heat of 26 such monatomic elements is 6.07 and at
50° is 6.28, but the actual values for the same elements range
between 5.41 and 6.76 at 0° and 5.66 and 7.33 at 50° C.
Boron, glucinum, and titanium, whose molecular condition
is not certainly known, give values greatly below the average
values above stated, as do carbon and silicon, while arsenic,
antimony, and bismuth, which have polyatomic molecules,
are in fair agreement with the averages given. In short,

at room temperature, considering the elements for which the best measurements exist, 30 elements show a range in the constant of Dulong and Petit's "law" of about 25 percent and seven other elements show greater divergence. At all other temperatures the disagreement is worse. The essential facts have been pointed out before, but everybody has been brought up to love the "law" from childhood.

The equation of Debeye gives the best reproduction of the specific heat lines of the solid elements of any equation yet proposed. The equation is highly complicated, its accuracy is still under investigation, and the correctness of the theoretical basis for the equation is doubtful. Nothing could be gained by its discussion here.

In Table 1 the elements are arranged in groups and a number of relations are shown.

The total energy added to a monatomic element from 0° *absolute to its melting point, including the heat of fusion, divided by the absolute temperature of the melting point is nearly the same as the specific heat of the liquid element at its melting point.* (See Table 1, columns headed "Heat at melting point," "Liquid" and "Average.") The importance of this observation lies in the fact that it shows that the *heat of fusion is merely supplementary to the specific heat of the solid* and that one could extrapolate the liquid condition to the absolute zero without great error so far as the energy content of the liquid is concerned. Thus the heat of fusion of sodium is fairly closely represented by the area (see Diagram 1) bounded by the specific heat curve of sodium, the ordinate axis, and a line drawn parallel to the temperature axis through the specific heat of liquid sodium.

The specific heat of the liquid is in many cases very uncertain and due allowance must be made for this uncertainty. The specific heat of the solid element at its melting point is also given, and it will be seen that it is usually *only slightly less* than the specific heat of the liquid. Perhaps the above relation also holds for the polyatomic elements and for compounds *when a correction has been made* to allow for certain other energy changes involved.

TABLE I

	Heat at melting point			Average gram atom	Total $\frac{}{Lf}$	$\frac{mLf}{T}$	$\frac{m\Sigma\sigma}{T}$	Total — $2E\kappa$	$\frac{mL\sigma}{T}$
	Solid	Liquid	Average						
Lithium	1.169	—	0.719	4.99	9.93	0.50	4.49	—439	—
Sodium	0.329	0.323	0.312	7.17	4.23	1.70	5.47	451	—
Potassium	0.191	0.184	0.195	7.63	4.49	1.70	5.93	562	—
Rubidium	0.0919	0.0911	0.0934	7.98	4.74	1.68	6.30	630	—
Caesium	0.0600	0.0595	0.0628	8.34	5.04	1.66	6.68	716	—
Copper	0.127	—	0.132	8.37	4.13	2.03	6.34	3275	27.2
Silver	0.0730	0.0748	0.0778	8.39	3.89	2.16	6.23	2998	25.7
Gold	0.0349	—	0.0431	8.50	3.53	2.41	6.09	3398	31.5
Magnesium	(0.298)	—	0.320	7.78	4.10	1.90	5.88	1682	33.8
Zinc	0.103	0.374	0.127	8.27	3.19	2.59	5.68	1598	22.9
Cadmium	0.0622	0.096	0.0744	8.36	3.23	2.59	5.77	1429	22.7
Mercury	0.0332	0.0339	0.0386	7.74	3.25	2.39	5.35	417	21.6
Aluminum	0.319	0.3081	0.304	8.23	3.45	2.39	5.84	2116	23.1
Gallium	—	—	—	—	—	4.41	—	—	—
Thallium	(0.0338)	—	0.0419	8.56	3.35	2.55	6.01	1492	—
Tin	(0.0657)	0.0637	0.0768	9.14	2.72	3.35	5.79	1608	27.9
Lead	0.0339	0.0406	0.0383	7.93	4.30	1.84	6.09	1185	24.3
Iron	0.167	—	0.189	10.54	4.93	2.14	8.40	8262	—
Palladium	0.0835	—	0.0862	9.20	4.33	2.13	7.07	5908	—
Platinum	0.0418	—	0.0490	9.56	3.65	2.61	6.95	7300	—
Hydrogen	—	—	—	3.47	3.01	1.16	2.31	7	5.38
Oxygen	—	0.347	0.354	5.67	1.67	3.07	2.07	147	9.03
Nitrogen	0.207	0.476	0.367	5.14	4.14	1.28	4.02	135	8.65
S. Rhombic	0.185	0.228	0.164	5.30	5.34	0.99	4.29	890	15.2
S. Monoclinic	0.199	0.228	0.164	5.28	1.84	4.80	4.04	891	15.2
Chlorine	0.170	0.212	0.249	8.84	2.03	4.87	5.01	994	10.3
Bromine	0.106	0.107	0.124	9.88	2.50	3.85	5.76	1833	10.9
Iodine	0.0570	0.108	0.0758	9.61	9.76	0.49	4.31	2565	6.6
Phosphorus	0.186	0.204	0.155	4.80	2.11	5.35	5.92	1048	14.4
Antimony	0.0608	—	0.0938	11.27	2.21	4.74	5.75	7486	—
Bismuth	0.0316	0.0363	0.0504	10.49	—	—	—	4087	24.4

[1] Glaser 0.391.

The total heat in a gram atomic weight of the liquid element at its melting point divided by the absolute temperature of the melting point is shown in Table 1 under the heading "Average gram atom." The value for lithium so obtained is below 5.96, apparently therefore an impossible value as will appear more clearly later. The data for lithium were widely divergent and the values adopted are almost certainly wrong. The average values given apparently increase with rise in the melting point and the value for tin is therefore out of line. The change in the allotropic form of iron with rise in temperature accounts partly for the high value there obtained. The average for the polyatomic elements at the melting point is apparently not so simple a function, but hydrogen and phosphorus are suspiciously out of line with what might be expected.

The ratio of the total heat in a gram atom of the liquid element at its melting point to the heat of fusion is given in Table 1 under the heading $\frac{\text{"Total"}}{L_f}$. Again lithium, tin, phosphorus and hydrogen are suspiciously out of line.

The next column, under the heading $\frac{\text{"}mL_f\text{"}}{T}$, contains the atomic heat of fusion divided by the absolute temperature of fusion. Again lithium, tin, phosphorus, and hydrogen are out of line. The value given by gallium seems high and that for lead low. It should be noticed that Roos adopts 6.37 calories per gram for the heat of fusion of lead and this value would make $\frac{mL_f}{T} = 2.19$.

Next under the heading $\frac{m\Sigma\sigma}{T}$ is given the quotient obtained by dividing the total atomic specific heat in the *solid* element at its melting point by the absolute temperature. Compare with Laemmeli's statement "Die integral Mittel der Atomwärmen der Elemente im festen Zustand sind gleich, und zwar ca. 6.5." The sum of the values in this column and those in the previous column equal the average per gram atom at the melting point already given. Lithium is out of line, and while several of the other values may be, they are

not strikingly wrong, indicating that it is probably the heats of fusion of tin, lead, phosphorus, hydrogen (and gallium and lithium also) that are either wrong or somewhat exceptional. The value of the heat of fusion of tin has often been determined and is probably correct. The other values mentioned should be investigated very carefully. *The values shown in this column are of particular interest because they are seldom much greater than 5.96 and indicate that those theories based upon the supposition that metallic electrons require notable specific heat energy are wrong. The atomic specific heat often greatly exceeds 5.96 as the tables given in Part I have shown, but the element probably always melts before the average energy from 0° absolute per atom at constant volume equals this amount.*

In the next to the last column of Table 1, under the heading "Total — $2E_K$," is given the difference between the total energy in a gram atomic weight of the liquid at its melting point and twice the kinetic energy of the substance at the same temperature, the kinetic energy E_K being calculated from the equation

$$1. \qquad E_K = {}^3\!/_2 \, \frac{RT}{m} = \frac{2.9791T}{m} \text{ calories per gram.}$$

In making this calculation for the polyatomic elements the following formulas were assumed: H_2, O_2, N_2, S_2, Cl_2, Br_2, I_2, P_4, Sb_2, Bi_2. Consequently the values may be greatly wrong for sulphur, antimony, and bismuth, and possibly have no great significance for the polyatomic elements. A better method of determining and comparing the effect of the attractive forces is shown later.

This difference, Total — $2E_K$, should not be negative. For the monatomic elements this difference is probably a fairly accurate measure of the energy required for expansion against the attractive forces throughout the interval 0° absolute to the melting point.

It will be noticed that some of the columns in Table 1 contain some very suggestive regularities. Just how far the irregularities may be due to the data used it is not possible to say and speculation would seem useless. My hope has

been that a discussion of all of the available data would so eliminate gross errors that a rational theory of the specific heat energy would become possible and I trust that this paper will prove that this hope is at least partially fulfilled.

In the last column of Table 1, under the heading $\frac{"mL_a"}{T}$, is shown the atomic heat of vaporization divided by the absolute temperature. The zero group gives values as follows: helium 4.65, argon 17.7, krypton 18.8, xenon 18.9, and niton 19.6. Also carbon = 37.3.

Part III

The energy added to a substance as its temperature is raised can be conveniently considered as energy spent in:

1. Overcoming the external pressure = E_E.

2. Increasing the kinetic translational motion of the molecule = E_K.

3. Overcoming the attraction between the molecules = E_a.

4. Increasing the internal motion of the atoms within the molecules = E_I.

5. Overcoming the chemical attraction between the atoms = E_c.

The total added energy is therefore $E_E + E_K + E_a + E_I + E_c$.

(1) The energy spent per gram in overcoming the external pressure can be calculated from the equation

2. $E_E = 0.0431833\ P(V - v)$ calories,

where the pressure is given in millimeters of mercury per square centimeter, and V and v denote the volumes of a gram of the substance after and before expansion. For solids and liquids the change in volume on expansion is so small that E_E can be considered zero for them.

(2) The energy spent per gram in increasing the translational motion of the molecules for a perfect gas is given by the equation

1. $E_K = {}^3/_2 \frac{RT}{m} = \frac{2.9791 T}{m}$ calories,

already given. The fact that a dissolved non-electrolyte in

dilute solution exerted the same pressure as osmotic pressure as would be exerted by the molecules of a perfect gas under the same conditions led the author and others to argue that the translational motion, and hence the kinetic energy, must be the same in the liquid as in the gaseous condition at the same temperature. This idea is, however, wrong. It seems likely that in the liquid condition, and therefore probably in the solid condition, the substance retains, due to the effect of the attractive forces, twice the kinetic energy that the same substance will retain as a gas under the same pressure and at the same temperature. Somewhat different explanations are given.

The author's idea is founded upon the fact that centrally acting attractive forces under the inverse square law necessitate that n particles in stable kinetic equilibrium retain as much kinetic orbital energy as they give out, if temperature energy is zero. See the original papers.[1] The retained orbital energy per gram E_o can be calculated from the equation

$$3. \qquad E_o = \mu' \sqrt[3]{d} \text{ calories,}$$

where μ' is a constant for each substance calculated as shown later, and d is the density of the substance. When the temperature is not zero the retained orbital energy is in the liquid condition, $\mu'^3\sqrt{d} + E_K$. The temperature energy is E_K. Hence, on lowering the temperature $2E_K$ is given out.

Or the following statement might be considered more clear by some. When n particles are in stable kinetic equilibrium under the action of central forces varying as the inverse square of the distance between the particles, the effect of increased temperature is to increase the major semi-axis of the orbits of the particles. Such increase requires the absorption of energy equivalent to the increase of kinetic temperature energy added.

It is possible to increase the major semi-axis without altering the volume. If the volume is altered a greater addi-

[1] Phil. Mag., 22, 84 (1911); Jour. Phys. Chem., 19, 657 (1915).

tion of energy than $2E_K$ is required, but this additional energy required to change the volume is rightly considered energy of expansion and is classed under E_a. The second explanation is essentially the same as the first, but involves an assumption as to the nature of the orbit—an assumption, however, that I believe is justified and necessitated by ordinary mechanical laws.

Hence for a substance in the liquid condition we have per gram

4.
$$E_K = \frac{3RT}{m} = \frac{5.96T}{m} \text{ calories.}$$

(3) In the series of papers to which this article belongs I have shown that the following equation holds true:

5.
$$\frac{L - E_E}{\sqrt[3]{d} - \sqrt[3]{D}} = \mu',$$

where L is the heat of vaporization per gram, E_E is the energy spent in overcoming the external pressure during the vaporization, d and D are the densities of liquid and vapor, respectively, and μ' is a constant for any particular substance. Abundant evidence of the truth of the equation has been published.

The equation was theoretically derived upon the assumption that the force of attraction varied directly as a constant and inversely as the square of the distance apart of the attracting particles. This theory would indicate that the energy required per gram to overcome molecular attraction during any given expansion could be obtained from the expression

6.
$$E_a = \mu' \left(\sqrt[3]{d_1} - \sqrt[3]{d_2} \right) \text{ calories,}$$

where d_1 and d_2 are the densities of the substance before and after expansion. It has not hitherto been possible to prove the truth of Equation 6 outside of the saturated vapor-liquid region for which Equation 5 was proved true. I will here assume its truth and proceed to see if the facts warrant the assumption.

(4) The well-known theory of Waterston gives the relation

7. $$\gamma = \frac{\sigma_p}{\sigma_v} = \frac{R + {}^3/_2\,R + E_I}{{}^3/_2 R + E_I} = \frac{5R + 2E_I}{3R + 2E_I}$$

for a perfect gas. Solving for E_I we get

8. $$E_I = \frac{R}{2} \cdot \frac{5 - 3\gamma}{\gamma - 1}.$$

Putting $R = {}^2/_3 E_K$ we have

9. $$E_I = \frac{1.666 - \gamma}{\gamma - 1} \cdot E_K.$$

Therefore for a perfect gas the energy which goes inside the molecule is proportional to the kinetic energy of the gas and can be calculated when γ has been measured.

For a monatomic gas E_I is always zero, γ being equal to 1.66, a relation which holds for the monatomic gases over all regions in which they have been investigated.

For polyatomic gases the relation is much more complex. Theory based upon the equipartition of energy—a theory upon which there is not unanimous agreement—indicates that

10. $$E_I = \frac{nR}{2m} = \frac{.993n}{m} \text{ calories per gram,}$$

where n is the number of atoms in the molecule. Hence the molecular specific heat at constant volume for a diatomic gas would be 4.96 and for a triatomic gas 5.96. For several of the most stable gases the actual value usually obtained is less than the value assigned above, but it must be remembered that the specific heat at constant volume varies with the volume, that is, with the pressure, to which the gas is subjected. It would seem probable that a pressure could always be chosen at which the molecular specific heat at constant volume would equal the assigned values and that the slight variations could be explained as a secondary variation due to the attractive forces, were it not for the recent experiments of Eucken with hydrogen at very low temperatures. Eucken finds that at such temperatures the hydrogen molecule be-

haves as a molecule of a monatomic gas. Further discussion can well await the substantiation of Eucken's results.

(5) For all polyatomic gases the specific heat at constant volume increases with the temperature until the molecule is broken down into its atoms. Since a part of the heat absorbed results finally in the decomposition of the molecule this part can be regarded as chemical energy going to over-come the attraction between the atoms of which the molecules are composed. The heat so absorbed seems to increase as the temperature of decomposition is approached and to approach zero with extremely stable molecules at low temperatures. E_I as calculated from Equation 9 will usually, therefore, contain some energy which should be classified as E_c. It is not yet possible to rely with confidence upon the truth of Equation 10, and there is as yet no method for calculating theoretically the chemical energy absorbed.

In view of the above facts our present knowledge can be expressed as follows:

For a monatomic gas or liquid, $E_I = 0$ and $E_c = 0$. For a polyatomic gas E_I is probably equal to $\frac{nR}{2m}$ (remembering that substantiation of Eucken's results may revise this conclusion) and $E_c = 0$, if the molecule is extremely stable, and $E_c > 0$ for less stable molecules, and gradually increases until the molecule decomposes.

I do not contend for the idea that chemical and molecular forces are necessarily different in their ultimate nature, but the distinction between atoms and molecules and therefore between E_a and E_c made in the foregoing discussion needs no defense here.

If the views above outlined are correct the total energy in a gram atomic weight of a liquid monatomic molecule at its melting point can be calculated with only slight error, as follows:

11. Total energy $= 2E_K + E_a = 5.96\ T +$
$$m\mu'(\sqrt[3]{d_0} - \sqrt[3]{d_{\text{M.P.}}})\ \text{calories,}$$

TABLE 2

	Boiling point — Density (Liquid)	Density (Vapor)	Volume (Liquid)	Volume (Vapor)	$\sqrt[3]{d}$	$\sqrt[3]{D}$	$\sqrt[3]{d}-\sqrt[3]{D}$	L	E_s	$L-E_s$	$\dfrac{L-E_s}{\sqrt[3]{d}-\sqrt[3]{D}}\mu'$
Helium	0.151	0.01133	6.623	88.26	0.5325	0.2246	0.3079	4.99	1.97	3.015	9.79
Argon	—	—	—	76.92	—	—	—	—	—	—	39.76*
Xenon	3.063	0.013	0.326	3330	1.4523	0.2351	1.2172	27.55	1.85	25.70	21.1
Copper	7.56	0.0_3300	0.132	1496	1.9626	0.0669	1.8957	1104	80.7	1023.3	540
Zinc	6.46	0.0_3668	0.155	258	1.8624	0.874	1.7750	417.6	36.2	381.4	215
Mercury	12.748	0.00388	0.078	6280	2.3360	0.1571	2.1789	67.8	6.24	61.56	28.2
Aluminum	2.01	0.0_3159	0.498	1760	1.2620	0.0542	1.2078	1771	151.9	1619.1	1340
Tin	5.75	0.0_3569	0.174	713	1.7917	0.0829	1.7089	597.1	42.5	554.6	324
Lead	9.26	0.00140	0.108	828.1	2.1000	0.1119	1.9881	211.0	17.2	193.8	97.5
Hydrogen	0.07086	0.001208	14.112	226.2	0.4138	0.1065	0.3073	108.6	19.7	88.9	289.3
Oxygen	1.1456	0.00442	0.873	219.9	1.0463	0.1641	0.8822	50.92	5.45	45.47	51.54
Nitrogen	0.8042	0.004548	1.243	272.9	0.9299	0.1657	0.7642	47.75	5.29	42.46	55.56
Chlorine	1.568	0.003664	0.638	172.6	1.1618	0.1542	1.0076	69.2	6.59	62.61	62.13
Bromine	2.9483	0.005793	0.339	371.7	1.4339	0.1796	1.2543	46.0	4.17	41.83	33.3
Phosphorus	1.485	0.00269	0.673	—	1.1409	0.1391	1.0018	130.4	8.97	121.43	121.2

* Average value from a series of observations.

where d_o is the density of the element at the absolute zero and $d_{M.P.}$ is the density at the melting point.

Before making this calculation it is necessary to calculate μ'. This calculation is made as shown by Equation 5, the necessary data and the results being shown in Table 2. The data not given in Part I of this paper have been for the most part obtained from Landolt, Börnstein and Roth's "Tabellen" and the "Tables Annuelles." The values for the density of the vapor at the boiling point have been calculated from the equation

12. $$D = \frac{0.0416027Pm}{T}.$$

The values of the density at $0°$ absolute given in Table 3 have been obtained by extrapolation either by myself or by others. The values of the density of the liquid at the melting point there given are from the tables cited. Using these values and the values of μ' given in Table 2, there are shown in Table 3 under the heading $2E_K + E_a$ the results of the calculation of the total energy in a gram atomic weight of the liquid at its melting point as given by Equation 11. The observed values are given under the heading "Observed."

The agreement between the calculated and the observed values for mercury, aluminum, tin and lead are quite as good as could be expected from the accuracy of the data at hand. For copper and zinc the divergence between the calculated and observed values is too great to be attributed to errors in the data without further experimental investigation. Therefore no final conclusion as to the correctness of the theory can be drawn, but the fact that substantial agreement is reached for four of the six metals for which the calculation was possible warrants a further extension of the theory. Fortunately this is possible in several ways, as shown below, and the results obtained, as will be seen, are such as to greatly strengthen belief in the substantial accuracy of the ideas advanced.

To test the idea advanced further we proceed next to *calculate the total energy in the vapor of mercury at its boiling*

, *J. E. Mills*

TABLE 3

Total heat in liquid at melting point

	Density		$\sqrt[3]{d_{o\,K}}$	$\sqrt[3]{d_{M.P.}}$	$\sqrt[3]{d_{o\,K}} - \sqrt[3]{d_{M.P.}}$	E_a	$2E_K$	Calculated $2E_K + E_a$	Observed
	Solid 0°K	Liquid Melting Point							
Copper	9.046	8.40	2.0836	2.0328	0.0508	1743	8082	9825	11357
Zinc	7.20	6.92	1.931	1.9056	0.0254	357	4126	4483	5724
Mercury	14.488	13.6902	2.4378	2.3922	0.0456	258	1396	1654	1813
Aluminum	2.751	2.41	1.4012	1.3407	0.0605	2198	5548	7746	7664
Tin	7.389	6.993	1.9477	1.9123	0.0354	1367	3008	4375	4616
Lead	11.616	10.875	2.265	2.2155	0.0495	999	3578	4577	4763

point, again making use of Equation 11 and substituting the density of the vapor at the boiling point for the density of the liquid at its melting point and adding the energy required to perform external work during the expansion. The data have already been given. The equation takes the form

14. Total energy in one gram atomic weight of mercury vapor at its boiling point $= 2E_K + E_a + E_E = 3RT + m\mu'$-$(\sqrt[3]{d_0} - \sqrt[3]{d_{B\,P.}}) + 0.0431833 \; P(V - v) = 3,752 + 12,926 + 1,252 = 17,930$ calories.

The above value is to be compared with the observed value of the total heat of a gram atomic weight of mercury vapor obtained from data previously given. Thus we have for energy added as

Specific heat of solid	=	1,254 calories
Heat of fusion	=	559 calories
Specific heat of liquid	=	2,634 calories
Heat of vaporization	=	13,600 calories
Total	=	18,047 calories

The agreement between the calculated and the observed value is certainly excellent. As is well known, the specific heat of mercury vapor appears to be exactly in accord with theory and hence the above simple explanation of the total heat in the vapor is of great theoretical interest.

It is well to point out that Equation 14 is subject to three slight errors. *First.* The molecules of solid mercury are probably not exactly uniformly distributed throughout the space they occupy. *Second.* The vapor pressure of mercury has a slight effect for which no allowance is made. *Third.* The attractive forces between the molecules of mercury vapor possibly introduce another error.

The ideas advanced enable the specific heat of liquid mercury to be calculated. The result of such an attempt is shown in Table 4. The calculation is again based on Equation 11 and the energy of attraction E_a is calculated from the change in density as before. Thus,

15. Specific heat of monatomic liquid $= 2E_K' + E_a =$
$$\frac{3R}{m} + \frac{\mu'(\sqrt[3]{d_1} - \sqrt[3]{d_2})}{t_2 - t_1},$$

TABLE 4.

Specific heat of liquid mercury

Temperature	Density	$\sqrt[3]{\bar{d}}$	Temperature	$\dfrac{\sqrt[3]{\bar{d_1}}-\sqrt[3]{\bar{d_2}}}{t_2-t_1}$	E_a	Calculated $2E_\kappa + E_a$	Observed specific heat
—10° C	13.62017	2.38815	0° C	0.0_3144	0.00407	0.03377	0.03350
10	13.57079	2.38526	—	—	—	—	—
40	13.4973	2.38094	50	0.0_3143	0.00403	0.03373	0.03307
60	13.4486	2.37808	—	—	—	—	—
90	13.3762	2.37380	100	0.0_3142	0.00400	0.03370	0.03289
110	13.3283	2.37096	—	—	—	—	—
190	13.1384	2.35965	200	0.0_3141	0.00398	0.03368	0.03292
210	13.0913	2.35683	—	—	—	—	—
290	12.9039	2.34553	300	0.0_3142	0.00400	0.03370	0.03336
310	12.8572	2.34269	—	—	—	—	—

where d_1 and d_2 are the densities of liquid mercury at the temperatures t_1 and t_2 chosen at equal temperature intervals below and above the temperature for which the specific heat is desired. The observed specific heat of liquid mercury given in Part I of this paper is shown in Table 4 for comparison with the calculated values. The agreement is probably not quite within the limit of experimental error of the data but is sufficiently close to confirm the general accuracy of the ideas advanced, as the slight divergences shown may be due to some of the sources of error mentioned in the preceding paragraph.

It should be pointed out that *the reciprocals of the distances apart of the molecules of liquid mercury between the temperatures —20° and 360° C decrease almost exactly linearly with the temperature.*

The author has heretofore published no *proof* that the inverse square law of molecular attraction could be extended beyond the saturated vapor liquid region for which the fundamental Equation 5 has been proved true.[1] *The calculations above made are evidence that the inverse square law of attraction holds true to the absolute zero both for liquid and solid.*

A density temperature diagram is shown for isopentane in Diagram 2. The relations there shown while not exact (the lines $d_0 d_3 d_4$ and $d_5 d_c d_4$ are not exactly straight and do
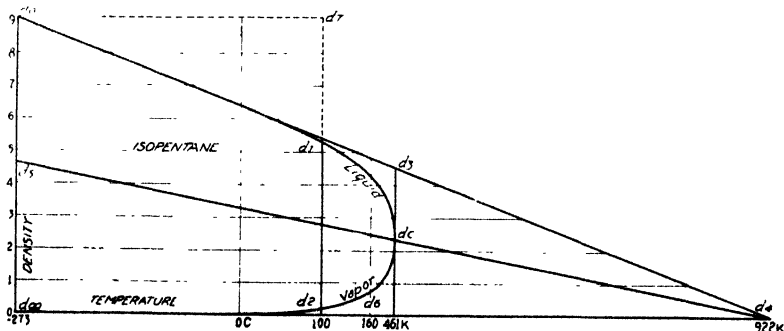
Diagram 2

[1] See series of articles in this Journal. Also Phil. Mag., Oct., 1910; July, 1911; Oct., 1912; Jour. Am. Chem. Soc., **31**, 1099 (1909).

not meet the temperature axis exactly at twice the critical temperature) seem to be approximately true for all substances. The ideas advanced indicate that the energy, exclusive of energy going to do external work, necessary to be added to change a monatomic element,

From d_0 to d_∞ = $\mu'^3\sqrt{\overline{d_0}}$ since density at d_∞ = 0.
" d_∞ to d_6 = E_K
" d_0 to d_7 = $2E_K$
" d_7 to d_1 = $\mu'(\sqrt[3]{d_0} - \sqrt[3]{d_1})$ since $d_7 = d_0$
" d_1 to d_2 = $\mu'(\sqrt[3]{d_1} - \sqrt[3]{d_2})$
" d_2 to d_6 = x

Starting with a monatomic element at the absolute zero and with a density d_0 it can theoretically be changed to a density d_2 at a temperature T along the path $d_0d_7d_1d_2$ or along the path $d_0d_\infty d_6d_2$, and the energy necessary to be added must be the same along either path. Therefore we have

16. $\mu'^3\sqrt{\overline{d_0}} + E_K - x = 2E_K + \mu'(\sqrt[3]{d_0} - \sqrt[3]{d_1}) + \mu'(\sqrt[3]{d_1} - \sqrt[3]{d_2})$
         whence $x = \mu'^3\sqrt{d_2} - E_K$,

where x is the energy necessary to change from the condition of saturated vapor at the temperature T to the condition of a gas at the same temperature whose molecules are theoretically at an infinite distance apart and hence in the condition of a perfect gas. This result is being further investigated.

It is not possible to test the value for x given above directly from existing specific heat data. But evidence that the argument given is in accord with the facts is obtained by calculating the total energy required to raise a gram molecule of some stable diatomic gases from 0° absolute to 0° C and comparing the calculated values with the observed. The calculation is made on the supposition that no energy will be given out in passing at 0° C from density d_∞ to density d_2 when $\mu'^3\sqrt{d_2}$ is less than E_K (see Equation 16) and d_2 represents the density of the gas under standard conditions of pressure and temperature. The internal energy and the energy necessary to do external work must be allowed for and the equation for the calculation takes the form:

17. Total energy at 0° C and 760 mm pressure for a

gram molecular weight of a stable gas $= E_E + E_K + E_I + E_a$. Here E_E is obtained from Equation 2, E_K from Equation 1, E_I from Equation 9, and $E_a = m\mu'^3\sqrt{d_0}$, where d_0 is the density of the solid at the absolute zero.

The values for this total energy for hydrogen, oxygen, nitrogen, and chlorine are shown in Table 5, and the observed values obtained from the data previously given are shown immediately beneath the calculated values. The data for nitrogen are much the most accurate and the agreement there obtained between the calculated and the observed values is very pleasing. For hydrogen and oxygen the agreement is as good as could be expected and for chlorine the data used are very unsatisfactory.

TABLE 5
Total energy at 0° C

	Hydrogen	Oxygen	Nitrogen	Chlorine
γ	1.407	1.400	1.4064	1.328
d_0	0.08333	1.5154	1.0984	2.147
$\sqrt[3]{d_0}$	0.4368	1 1486	1.0318	1.2901
E_E	542.0	541.1	541.6	540.8
E_K	813.3	813.3	813.3	813.3
E_I	518.7	542.1	520 7	837.7
E_a	254.6	1894.5	1606 6	5684.4
$E_E + E_K + E_I + E_a$	2129	3791	3482	7876
Observed	1849	3889	3469	9239

The total energy in a complicated polyatomic substance could presumably also be calculated according to Equation 17 if there were no change of chemical energy, E_c, to be considered.

In considering the value of the ideas advanced in Part III of this paper it should be noted that the data are most accurate for mercury and nitrogen and that those substances give a very satisfactory agreement with the theory.

Summary

1. Some atomic specific heat curves are shown and discussed.

2. The total energy added to a monatomic element from o° absolute to its melting point, including the heat of fusion, divided by the absolute temperature of the melting point, is nearly the same as the specific heat of the liquid element at its melting point.

3. Therefore the heat of fusion is supplementary to the specific heat of the solid, and the specific heat of a liquid monatomic element can be extrapolated to the absolute zero without great error so far as the total energy content of the liquid is concerned.

4. Atoms of monatomic elements in the liquid condition at their melting point T contain an amount of energy *approximately* proportional to the temperature (usually between 7.5 T and 8.5 T calories per gram atomic weight).

5. Those theories based upon the supposition that metallic electrons require notable specific heat energy are wrong.

6. The total energy added to a substance can be accounted for as being used in the following ways: to perform external work, to increase translational motion, to overcome molecular attractive forces, to increase motion within the molecule, and to overcome chemical forces of attraction. It is shown how the energy required for these different purposes (except the last) may be calculated. As proof of the correctness of the ideas advanced the total energy in a gram atomic weight of copper, zinc, mercury, aluminum, tin and lead, in the molten condition at their melting points, is calculated. Also the total heat in mercury vapor at its boiling point. Also the specific heat of liquid mercury. Also the total heat in a gram molecular weight of hydrogen, oxygen, nitrogen, and chlorine gas under standard conditions. The calculated values are compared with the observed. The agreement is satisfactory except for copper, zinc and chlorine where the divergences may be due to the data used.

7. If the divergences mentioned above are explainable as due to incorrect data, then the inverse square law of attraction holds true for molecular forces to the absolute zero for both liquid and solid.

8. The relation given in Equation 16 is derived.

9. The reciprocals of the distances apart of the molecules of liquid mercury between the temperatures — 20° and 360° C decrease almost exactly linearly with the temperature.

10. The heats of fusion of lead, phosphorus, hydrogen, gallium and lithium should be redetermined. Also certain data for copper, zinc, chlorine, and oxygen. Also it might be pointed out that a thorough experimental investigation of the energy changes of the liquids which Dr. Sidney Young has studied so carefully would prove of far greater benefit than ten times as much work spent in making heat measurements on miscellaneous liquids.

University of South Carolina
Columbia, S. C.
May 15, 1917

CONTACT CATALYSIS. II

BY WILDER D. BANCROFT

Fractional Combustion

The selective action of the catalytic agent is shown admirably in the fractional combustion of gases, though the data are by no means so complete as one would like. A very interesting study of the effect of platinum on the fractional combustion of gases was made by Henry[1] over ninety years ago; and it is still of fundamental importance.

"Several years have elapsed since the President of the Royal Society [Sir Humphry Davy], in the further prosecution of those researches on flame which had already led him to the most important practical results, discovered some new and curious phenomena in the combustion of mixed gases, by means of fine wires of platinum introduced into them at a temperature below ignition. A wire of this sort being heated much below the point of visible redness, and immersed in a mixture of coal gas and oxygen gas in due proportions, immediately became white-hot, and continued to glow until all that was inflammable in the mixture was consumed. The wire, repeatedly taken out of the mixture and suffered to cool below the point of redness, instantly recovered its temperature on being again plunged into the mixed gases. The same phenomena were produced in mixtures of oxygen with olefiant gas, with carbonic oxide, with cyanogen, and with hydrogen; and in the last case there was an evident production of water. When the wire was very fine, and the gases had been mixed in explosive proportions, the heat of the wire became sufficiently intense to cause them to detonate. In mixtures which were non-explosive from the redundancy of one or other gas, the combination of their bases went on silently, and the same chemical compounds were formed as by their rapid combustion.

[1] Phil. Mag., 65, 269 (1825).

"Facts analogous to these were announced in the autumn of last year by Professor Doebereiner, of Jena, with this additional and striking circumstance— that when platinum in a spongy form is introduced into an explosive mixture of oxygen and hydrogen, the metal, even though its temperature had not been previously raised, immediately glows, and causes the union of the two gases to take place, sometimes silently, at others with detonation. It is remarkable, however, that platinum in this form, though so active on mixtures of oxygen and hydrogen, produces no effect, at common temperatures, on mixtures of oxygen with those compound gases, which were found by Sir Humphry Davy to be so readily acted upon by the heated wire. Carbonic oxide appears indeed, from the statement of M.M. Dulong and Thenard, to be capable of uniting with oxygen at the temperature of the atmosphere, by means of the sponge; but though this is in strictness true, yet the combination, in all the experiments I have made, has been extremely slow, and the due diminution of volume has not been completed till several days have elapsed. On mixtures of olefiant gas, of carburetted hydrogen, or of cyanogen, with oxygen, the sponge does not by any duration of contact exert the smallest action at common temperatures.

"It was this inefficiency of the platinum sponge on the compounds of charcoal and hydrogen in mixture with oxygen, while it acts so remarkably on common hydrogen, and also, though slowly, on carbonic oxide, that suggested to me the possibility of solving by its means some interesting problems in gaseous analysis. I hoped more especially to be able to separate from each other the gases constituting certain mixtures, to the compositions of which approximations only had been hitherto made, by comparing the phenomena and results of their combustion with those which ought to ensue, supposing such mixtures to consist of certain hypothetical proportions of known gases. It might, for instance, be expected that from a mixture of hydrogen and carburetted hydrogen with oxygen, the platinum sponge would cause the removal of the hydrogen, leaving the carburetted hydrogen

unaltered. To ascertain this and a variety of similar facts, I made artificial mixtures of the combustible gases in known volumes; and submitted them, mixed with oxygen, sometimes to contact with the sponge, and sometimes with the balls of clay and platinum, described by Professor Doebereiner.

"When to equal volumes of olefiant gas and an explosive mixture (which is to be understood, whenever it is so named, as consisting of two volumes of hydrogen and one of oxygen gases), one of the platinum balls, recently heated by the blow-pipe, and allowed to cool during eight or ten seconds, is introduced through mercury, a rapid diminution of volume takes place; the whole of the hydrogen and oxygen gases is condensed; but the olefiant gas is either not at all or very little acted upon. In a few experiments when the tube was narrow, and the quantity of mixed gases small, the olefiant gas escaped combustion entirely; but, in general, an eighth or tenth of it was converted into water and carbonic acid. It is difficult, however, to state the precise proportion of any gas which, when added to an explosive mixture, renders the latter insensible to the action of the balls or sponge; for much depends on their temperature when introduced into the gaseous mixture, the diameter of the containing vessel, and other circumstances, which, in comparing different gases, should be so regulated as to be equal in every case.

"When the proportions of the gases are changed, so that the explosive mixture exceeds in volume the olefiant gas, there is a more decided action upon the latter, manifested by an increased production of carbonic acid. Thus, for example, the explosive mixture being to the olefiant as 2.5 to 1, about one-fourth of the olefiant gas was consumed; and by increasing the proportion of the explosive mixture the olefiant gas was still more acted upon. On using oxygen sufficient to saturate both the hydrogen and the olefiant gases, the ball acted much more rapidly: in several instances it became red-hot; all the hydrogen was consumed; and the whole of the olefiant gas was changed into water and carbonic acid. In

this case the use of the sponge is inadmissible, as it kindles the gases, and occasions their detonation.

"When carburetted hydrogen, procured from stagnant water, was added to an explosive mixture, in various proportions between equal volumes, and ten of the former to one of the latter, the action of the hydrogen and oxygen on each other took place as usual, on admitting one of the balls. When, reversing the proportion, the explosive mixture was made to exceed the carburetted hydrogen, but not more than four or five times, the latter gas was entirely unchanged. With a larger proportion of the explosive mixture carbonic acid was always found to have been produced; but still the carburetted hydrogen was very imperfectly consumed; and fully three-fourths of it were generally found to have escaped unburned.

"When to a mixture of hydrogen and carburetted hydrogen, oxygen enough was added to saturate both gases, the effect of the sponge was found to vary with the proportion of the simple hydrogen. In several cases, where the hydrogen did not exceed the carburetted hydrogen more than four times, the latter gas remained unchanged; when in larger proportion, there was a decided action upon the carburetted hydrogen. But it was much more easy to regulate the action of the balls upon such a mixture so as to act upon the hydrogen and oxygen only, than in the case of olefiant gas, which, under similar circumstances, is always more largely converted into water and carbonic acid.

"The addition of one volume of carbonic oxide to two volumes of an explosive mixture produces a distinct effect in suspending the action of the platinum balls, and even of the spongy metal itself. The action of the gases upon each other still, however, goes on slowly, even when the carbonic oxide exceeds the explosive mixture in volume; and after the lapse of a few days the oxygen is found to have disappeared, and to have partly formed water, and partly carbonic acid. I made numerous experiments to ascertain whether the oxygen, under those circumstances of slow combustion, is divided between

the carbonic oxide and the hydrogen in proportions corresponding to the volumes of those two gases. The combustible gases being in equal volumes, and the oxygen sufficient to saturate only one of them, it was found that the oxygen which had united with the carbonic oxide was to that which had combined with the hydrogen as about 5 to 1 in volume. Increasing the carbonic oxide, a still larger proportion of oxygen was expended in forming carbonic acid. On the contrary, when the hydrogen was increased, a greater proportional quantity of oxygen went to the formation of water. But it was remarkable that, when the hydrogen was made to exceed the carbonic oxide four or five times, less oxygen in the whole was consumed than before; the activity of the carbonic oxide appearing to have been diminished, without a corresponding increase in that of the hydrogen.

"In cases where the proportion of the carbonic oxide to the explosive mixture was intentionally so limited that the platinum ball was capable of immediately acting upon the latter, the carbonic oxide was always in part changed into carbonic acid, the more abundantly as its volume was exceeded by that of the explosive mixture. Increasing the oxygen, so that it was adequate to saturate both gases, and causing the hydrogen to exceed the carbonic acid in volume, a speedy action was always exerted by the ball, and the whole of the combustible gases was silently converted into water and carbonic acid. The introduction of the platinum sponge into such a mixture was almost always found to produce detonation.   .   .   .

"It had already been ascertained by Professor Doebereiner that one volume of oxygen diluted with 99 volumes of nitrogen is still sensible, when mixed with a due proportion of hydrogen, to the action of the sponge. Carbonic acid also, even (I find) when it exceeds the explosive mixture ten times, retards only in a slight degree the energy of the sponge. Oxygen, hydrogen, and nitrous oxide gases, when employed to dilute an explosive mixture, are equally inefficient in preventing the mutual action of its ingredients. Ammonia may

be added in ten times the volume of the explosive mixture, and muriatic acid gas in six times its volume, with no other effect than that of rendering the action of the sponge less speedy.

"When mixtures of these gases are exposed to the sponge, the carburetted hydrogen seems to stand entirely neutral. The carbonic oxide is converted into carbonic acid, in the same gradual manner as if it had been mixed with oxygen only; and the carburetted hydrogen remains unaltered.

"In mixtures of these gases, it is of little consequence whether the oxygen be sufficient for the hydrogen and carbonic oxide only, or be adequate to the saturation of all three. The circumstance which has the greatest influence on the results of exposing such mixtures to the sponge, is the proportion which the simple hydrogen bears to the other gases, and especially to the carbonic oxide; for in order that there may be any immediate action, the former should exceed the latter in volume. In that case the hydrogen is converted into water, and the carbonic oxide into carbonic acid; but the carburetted hydrogen, unless the excess of hydrogen be very considerable, remains unaltered. If the proportion of hydrogen be so small that no immediate action is excited by the sponge, the ingredients of the mixture nevertheless act slowly upon each other; and after a few days the whole of the hydrogen and carbonic oxide are found to have united with oxygen, and the carburetted hydrogen to remain of its original volume.

"When the oxygen, in a mixture of these gases, is sufficient to saturate the two first only, and the proportion of hydrogen is so adjusted that the action of the sponge is not very energetic, the hydrogen and carbonic oxide only are acted upon; but if the diminution of volume, which the sponge produces, be rapid and considerable, part of the olefiant gas is converted into water and carbonic acid. This effect on olefiant gas takes place still more readily if the oxygen present be adequate to the saturation of all three combustible gases.

"It is remarkable that, if to a mixture of hydrogen, carbonic oxide, and oxygen, in such proportions that the

sponge would act rapidly in producing combination, olefiant gas be added, the action of the gases on each other is suspended. Thus 20 measures of carbonic oxide, 31 of hydrogen, and 20 of oxygen were instantly acted upon by the sponge; but the addition of 20 measures of olefiant gas to a similar mixture entirely suspended its efficiency. By standing fourteen days, rather more than half the carbonic oxide was acidified, and about one-twelfth of the hydrogen was changed into water, but the olefiant gas remained unaltered.

"In mixtures of these four gases with oxygen, it was found by varying the proportion of hydrogen, that hydrogen and carbonic oxide are most easily acted upon; then olefiant gas; and carburetted hydrogen with the greatest difficulty. When the action of the sponge was moderate, only the hydrogen and carbonic oxide were consumed, or at most the olefiant gas was but partially acted upon. Adding more hydrogen, so as to occasion a more rapid diminution, the olefiant gas also was burned; but the carburetted hydrogen always escaped combustion, unless the hydrogen were in such proportion that the ball or sponge became red-hot.

"From the facts which have been stated, it appears that when the compound combustible gases, mixed with each other, with hydrogen, and with oxygen, are exposed to the platinum balls or sponge, the several gases are not acted upon with equal facility; but that carbonic oxide is most disposed to unite with oxygen; then olefiant gas; and lastly, carburetted hydrogen. By due regulation of the proportion of hydrogen, it is possible to change the whole of the carbonic oxide into carbonic acid without acting on the olefiant gas or carburetted hydrogen. With respect indeed to olefiant gas, this exclusion is attended with some difficulty, and it is generally more or less converted into carbonic acid and water. But it is easy, when olefiant gas is absent, so to regulate the proportion of hydrogen, that the carbonic oxide may be entirely acidified, and the whole of the carburetted hydrogen be left unaltered. This will generally be found to have been accomplished, when the platinum ball has occasioned a diminution of the mixture, at

about the same rate as atmospheric air is diminished by nitrous gas when the former is admitted to the latter in a narrow tube."

Hydrogen is adsorbed by platinum more strongly than ethylene and consequently it tends to burn first. Since ethylene does not burn at all under the same circumstances, it is possible, though not probable, that the combustion in presence of hydrogen may be due to the oxygen passing through some intermediate stage in which it oxidizes the ethylene. That would make this an induced reaction. It seems to me more probable that we are dealing with a case of local heating, the ethylene burning in presence of platinum at the higher temperature thus produced. This is the more probable since more ethylene is burned the greater the ratio of oxy-hydrogen gas and the greater the ratio of oxygen. In fact Henry found that ethylene, when mixed with sufficient oxygen, began to burn in contact with platinum sponge at about 250° and was converted completely into carbon dioxide at about 270°.

Lunge and Harbeck[1] have shown that carbon monoxide is retained very tenaciously by platinum and consequently we should expect it to burn before hydrogen and so it does. Methane is undoubtedly adsorbed much less by platinum than either hydrogen or carbon monoxide and this is in line with the fact that it is burned less readily under these circumstances. Henry found that methane and oxygen begin to react in presence of platinum sponge at temperatures just above 290°. He next studied the behavior of finely divided platinum at high temperatures on those mixtures of gases which are either not decomposed or are decomposed slowly at the temperature of the atmosphere.

"When carbonic oxide and hydrogen gases, in equal volumes, mixed with oxygen sufficient to saturate only one of them, were placed in contact with the sponge, and gradually heated in a mercurial bath, the mixture ceased to expand between 150° and 155°, and soon began to diminish in volume. On raising the temperature to 170°, and keeping it some

[1] Zeit. anorg. Chem., **16,** 50 (1898).

time at that point, no further diminution was at length perceptible. From the quantity of carbonic acid remaining at the close of the experiment, it appeared that four-fifths of the oxygen had united with the carbonic oxide, and only one-fifth with the hydrogen. When four volumes of hydrogen, two of carbonic oxide, and one of oxygen, were similarly treated, the hydrogen, notwithstanding its greater proportional volume, was still found to have taken only one-fifth of the oxygen, while four-fifths had combined with the carbonic oxide. These facts show that at temperatures between 150° and 170°, the affinity of carbonic oxide for oxygen is decidedly superior to that of hydrogen; as, from the experiments before described, appears to be the case, also, at common temperatures.

"But a similar distribution of oxygen, between carbonic oxide and hydrogen, does not take place, when those three gases are fired together by the electric spark. This will appear from the following table, in which the three first columns show the quantities of gases that were fired, and the two last, the quantities of oxygen that were found to have united with the carbonic oxide and with the hydrogen.

TABLE I

Volumes before firing			Volumes formed	
CO	H_2	O_2	CO_2	H_2O
40	40	20	12	28
40	20	20	24	16
20	40	20	10	30

"When equal volumes of carbonic oxide and hydrogen gases, mixed with oxygen sufficient to saturate only one of them, were exposed in a glass tube to the flame of a spirit lamp, without the presence of the sponge, till the tube began to soften, the combination of the gases was effected without explosion, and was merely indicated by a diminution of volume and an oscillatory motion of the mercury in the tube.

At the close of the experiment, out of twenty volumes of oxygen, eight were found to have united with the carbonic oxide, and twelve with the hydrogen—proportions which do not materially differ from the results of the first experiment in the foregoing table. At high temperatures, then, the attraction of hydrogen for oxygen appears to exceed that of carbonic oxide for oxygen: at lower temperatures, especially when the gases are in contact with the platinum sponge, the reverse takes place, and the affinity of carbonic oxide for oxygen prevails. . . .

"Extending the comparison to the attraction of olefiant and hydrogen gases for oxygen at a red heat, I found that when six volumes of olefiant, six of hydrogen, and three of oxygen were heated by a spirit lamp till the tube softened, a slight combination took place as before; all the oxygen was consumed, but only half a volume had been expended in forming carbonic acid, which indicated the decomposition of only one-quarter of a volume of olefiant gas. On attempting a similar comparison between carbonic oxide and olefiant gas, by heating them with oxygen in the same proportions, the mixture exploded as soon as the glass became red-hot, and burst the tube.

"From the fact that carbonic oxide, olefiant gas, and carburetted hydrogen, when brought to unite with oxygen by means of the platinum sponge, assisted by heat, undergo this change at different temperatures, it seemed an obvious conclusion that by exposing a mixture of those gases with each other and with oxygen to a regulated temperature, the correct analysis of such mixtures might probably be accomplished. Mixtures of two or more of the combustible gases were therefore exposed, in contact with oxygen gas and the platinum sponge, in tubes bent into the shape of retorts, which were immersed in a mercurial bath. This bath was gradually heated to the required temperatures, and by proper management of the source of heat was prevented from rising above that degree.

"By subjecting 25 measures of carbonic oxide, 15 of

olefiant gas, and 57 of oxygen, in contact with the sponge, to a heat which was not allowed to exceed 175° till the diminution of volume ceased, all the carbonic oxide was converted into carbonic acid, and the olefiant gas remained in its original volume. By exposing in a similar manner 20 measures of carbonic oxide, 21 of carburetted hydrogen, and 36 of oxygen, to a temperature below 205°, the carbonic oxide was entirely acidified; and on washing out the carbonic acid by liquid potash, the carburetted hydrogen was found unaltered, mixed with the redundant oxygen. A mixture of 10 measures of olefiant gas, 10 of carburetted hydrogen, and 58 of oxygen being heated in contact with the sponge to 265°, the olefiant gas was silently but entirely changed into carbonic acid, while the carburetted hydrogen was not at all acted upon. By acting with the sponge upon 42 measures of carburetted hydrogen, 22 of carbonic oxide, 22 of hydrogen, and 28 of oxygen, first at a temperature of 170°, which was raised gradually to 250°, all the carbonic oxide was changed into carbonic acid, and all the hydrogen into water; but the carburetted hydrogen remained undiminished in quantity, and was found, after removing the carbonic acid, mixed only with the redundant oxygen. In this experiment the diminution of volume had continued some time before there was any perceptible formation of water, the attraction of carbonic oxide for oxygen appearing to prevail over that of hydrogen. The same precedency in the formation of carbonic acid is always apparent when carbonic oxide and hydrogen, mixed even with oxygen enough to saturate both gases, are raised to 175°.

"By thus carefully regulating the temperature of the mercurial bath, the action of oxygen upon several gases (carbonic oxide, olefiant, and carburetted hydrogen, for example) may be made to take place in succession; and by removing the carbonic acid formed at each operation, it may be ascertained how much of each of the two first gases has been decomposed. The carburetted hydrogen indeed always remains unchanged, and its quantity must be determined by

firing it with oxygen by the electric spark. If hydrogen also be present, it is difficult to prevent the olefiant gas from being partially acted upon; but this is of little consequence, as I had shown that it is easy to remove that gas in the first instance by chlorine. It may be remarked that this method of operating on the aeriform compounds of charcoal gives more accurate results than rapid combustion by the electric spark, being never attended with that precipitation of charcoal which is often observed when the gases are exploded with oxygen. A regulated temperature also effects the analysis of such mixtures much more correctly than the action of the sponge or balls, because in the latter case the heat produced is uncertain; and though sometimes adequate to the effect, yet there is always a risk that it may exceed or fall short of that degree which is required for the successful result of the analytic process."

This method of Henry's was afterwards worked out in more detail by Hempel[1] substituting palladium for platinum. A mixture of hydrogen with an excess of oxygen burns completely when passed over palladium. The reaction begins spontaneously at ordinary temperatures but so much heat is evolved that the palladium glows and the gases explode in case they are present in the ratio to form water. When methane and oxygen are passed over palladium at 100° no combination takes place. The reaction starts at about 200°. Thus there was a contraction of 3 cc when a mixture of 29.3 cc methane and 70.6 cc oxygen was passed several times over palladium at about 200°-220°. When a mixture of hydrogen, methane, and air is passed over palladium at ordinary temperatures or at 100°, the hydrogen alone is burned and the methane remains unchanged, provided precautions are taken so that the palladium does not heat up too much.[2]

If a mixture of hydrogen and methane is passed over copper oxide at 250°, the hydrogen is burned completely while

[1] Ber. deutsch. chem. Ges., **12**, 1006 (1879).
[2] Cf. Hempel: Zeit. angew. Chem., **25**, 1841 (1912).

the methane is not oxidized at all.[1] This method is said[2] to be distinctly superior to the fractional combustion of hydrogen by palladium or palladium asbestos because no air or oxygen is added to the combustible gas, which makes it possible to pass the total gas residue through the tube with consequent gain in the accuracy of the analytical results.

In view of the comparative readiness with which methane can be separated from hydrogen by the fractional combustion of the latter gas, it is not surprising that people came to the conclusion that hydrogen always burns more readily than methane. From experiments on the burning of illuminating gas, Landolt[3] concluded that in the flame "the gases disappear in the order of their combustibility. Hydrogen burns more readily than any other gas and consequently disappears the soonest in the flame. Marsh gas disappears somewhat more slowly, and the denser hydrocarbons disappear latest, burning chiefly in the upper half of the flame." It has been pointed out by Bone[4] that Landolt's results are vitiated by the fact that he used a platinum tube of narrow bore, fixed along the vertical axis of the flame for the withdrawal of the partly burned products.

Henry's experiments showed that carbon monoxide was burned before hydrogen when in contact with platinum at relatively low temperatures and that hydrogen burned before carbon monoxide when the gases were exploded by an electric spark. This last result is confirmed by Bunsen's experiments[5] given in Table II. More hydrogen is burned than carbon monoxide until the ratio of the second to the first is at least six. Henry[6] is quite explicit that the preferential burning of carbon monoxide in presence of platinum at $150°-170°$ and the preferential burning of hydrogen when the gases are

[1] Jäger: Jour. Gasbeleuchtung, **41**, 764 (1898).

[2] Dennis: "Gas Analysis," 199 (1913).

[3] Pogg. Ann., **99**, 411 (1856).

[4] Phil. Trans., **215**, 297 (1915).

[5] Bunsen: Ges. Abh., **2**, 586 (1904).

[6] Phil. Mag., **65**, 277 (1825).

fired by the electric spark is merely a question of temperature. Presumably Bunsen and Landolt held the same view because they do not comment on the low temperature results, which they probably would have done had they considered these results abnormal.

TABLE II

Volumes before firing			Ratio of $H_2O:CO_2$
CO	H_2	O_2	
7.36	2	1	0.85
5 98	2	1	1 08
4.87	2	1	1.28
5.03	2	1	1 29
3.90	2	1	1 53
2.82	2	1	1 83

A new light has been thrown upon the phenomena by Bone[1] and his co-workers. Bone was primarily interested in the way in which a hydrocarbon burns in a supply of oxygen insufficient to oxidize it completely to carbon monoxide, and steam; but, as is usually the case, the scope of the investigations soon became much broader. "The reasons for the selection of methane as the most suitable hydrocarbon for these studies were as follows: (1) it is the simplest saturated hydrocarbon and its molecule contains only one carbon atom; (2) preliminary experiments showed that it can be maintained at 480° to 500° (temperatures considerably higher than those afterwards employed in the oxidation studies) for many days without undergoing the least change; and (3) a mixture of two volumes of methane with one of oxygen is non-explosive. This was the mixture used throughout our experiments.

"In a preliminary series of experiments, the object of which was to determine the most suitable experimental methods for the inquiry, the mixture of methane (2 vols) and oxygen (1 vol) was circulated through a tube containing

[1] Jour. Chem. Soc., **81,** 535 (1902) et ff.

fragments of unglazed porcelain maintained at a constant temperature (between 400° and 450°) in a Lothar Meyer furnace. The apparatus involved, however, proved too complicated for experiments which necessarily extended over several days continuously; the results, it may be stated, indicate that a portion of the methane was burnt to carbon monoxide, carbon dioxide, and steam without any liberation of free hydrogen or carbon. We also tried maintaining the mixture at 300° to 350° in contact with palladium black but the 'catalytic' effect of the metal introduced complications which made it difficult for us to follow the real cause of the reaction.

"We finally resorted to the simple expedient of sealing the mixtures of methane and oxygen, under atmospheric pressure, in cylindrical bulbs of boro-silicate glass with capillary ends; the bulbs were afterwards maintained at constant temperatures (between 300° and 400°) for several days in an air-bath until the whole or a part of the oxygen had disappeared. The cooled bulbs were subsequently opened under mercury, any change in volume (always a·contraction) noted, and the residual gas withdrawn for analysis. We were thus able to examine the gases at various periods during the oxidation of the methane at any given temperature, and we could hardly fail to detect the formation of a product at any stage of the oxidation which afterwards disappeared before the process was completed.

"The interaction of two such gases as methane and oxygen in glass vessels at low temperatures being a surface phenomenon, the temperature at which its velocity is just appreciable, as well as the velocity at any other given temperature, will, to a certain extent, depend on the character of the surface. In our experiments, 300° was the lowest temperature at which any interaction could be detected after the lapse of two or three weeks. At 325°, however, the velocity was much greater; at 350°, in some instances, the whole of the oxygen disappeared within three or four days, while at 400° the oxidation was always completed in a single

day. But we have so far been unable to measure the relative velocities of the reaction at different temperatures on account of the fact that, except at 400°, when the velocity is considerable the influence of the 'surface factor' may be very different even in two bulbs of the same size, shape, and material. Thus, between 325° and 350°, an appreciable amount of oxidation always occurred within three days, but of a series of similar bulbs filled with the same mixture and heated in the same bath, some exhibited a greater amount of oxidation in two or three days than others did in a week or more. Nor does the 'surface factor' of a given bulb remain constant over two or three successive experiments with the same mixture; whether it would finally become constant after a long series of experiments is a point we are now investigating. . . .

"A series of experiments with bulbs similar to those used in the oxidation studies has shown that steam and carbon monoxide can be maintained at 325° for a fortnight without the slightest change occurring. At 350° no action could be detected within a week, but after tén days some 1.7 percent of carbon dioxide had been formed; at 400° about the same amount of change occurred in a week. On the other hand, mixtures of equal volumes of hydrogen and carbon dioxide showed no signs of change when kept at 325° or 350° for a fortnight or at 400° for a week. . . ."

We have found that moderately dry carbon monoxide and oxygen do not react between 300° and 400°; the formation of between 0.7 and 1.7 percent of carbon dioxide could usually be detected when the *moist* gases were maintained at 325°, 350°, or 400° for a week. The effects of this possible secondary change in the methane experiments are therefore practically negligible.

"In 1895 V. Meyer and Raum[1] published the results of an investigation on the combination of the elements of electrolytic gas in glass bulbs, very similar to those used by us, at temperatures between 300° and 518°. At 300°, the formation

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[1] Ber. deutsch. chem. Ges., **28**, 2804 (1895).

of water could just be detected after 65 days; in the case of
four out of five bulbs maintained at 350° for 5 days, a very
small amount of combination occurred (between 0.5 and 1.9
percent only of the original gas had disappeared), while in the
fifth bulb as much as 16.4 percent of the gases had combined.[1]
At 448°, the combination was still very slow. We have
carefully repeated these experiments, using bulbs which had
previously been employed for heating the mixtures of methane
and oxygen. At 335° we have never been able to detect the
slightest formation of water from electrolytic gas within a
week; at 350°, in six bulbs no combination took place in a
week, although in the case of a seventh bulb, in which the glass
had become devitrified at one end, the formation of water
could be distinctly seen. At 400° three bulbs exhibited no
signs of change after three days; after a week, water could be
distinctly seen in one bulb (nearly 40 percent of the mixture
had combined) but none could be detected in the other two.
Professor Dixon informs us that some years ago he main-
tained bulbs filled with electrolytic gas at 350° for several
weeks, but was unable to detect any formation of water.
Our own experience shows that hydrogen and oxygen, even
when mixed in combining proportions and undiluted with other
gases, do not within a week or two combine at 350° to any
appreciable extent provided the glass surface with which the
gases are in contact remains perfectly smooth. At 400°,
however, we are on the border line where the formation of
water may be recognized within a week but hardly within
three days. In our experiments with methane at this tem-
perature, the whole of the oxygen always disappeared within a
single day.

"We have also found that the following pairs of gases
have no mutual action at temperatures between 350° and
400° (within a week or two): methane and carbon dioxide;

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[1] Judging from our own experiments at this temperature, we are inclined
to attribute this relatively large formation of water to some roughness of the
inner surface of the bulb either present originally or caused by a partial devitrifica-
tion of the glass during heating.

methane and steam; carbon monoxide and hydrogen; it may therefore be taken for granted that no appreciable complication arising from possible secondary change enters into our experiments on the oxidation of methane.

"We have found that between 300° and 400° methane combines with oxygen with an enormously greater velocity than does hydrogen itself under the same conditions."

In a later paper Bone[1] says that "under similar conditions ethane burns much more rapidly than methane, and in borosilicate glass bulbs both hydrocarbons are oxidized at temperatures much below the limiting temperature (about 400°) at which, under similar conditions, steam is formed appreciably from electrolytic gas."

In a lecture before the Royal Institution Bone[2] showed an experiment "designed to illustrate the infinitely greater affinity of acetylene and ethylene as compared with that of hydrogen for oxygen at the high temperature of flames. I have here two bulbs containing mixtures of each of these hydrocarbons with hydrogen and oxygen corresponding to $C_2H_2 + 2H_2 + O_2$ and $C_2H_4 + H_2 + O_2$, respectively, and I will ask you to contrast the behavior of these with that of the equimolecular mixture of ethane and oxygen $C_2H_6 + O_2$ which was exploded a few minutes ago. It should be noted that while all three mixtures contain the same relative proportions of carbon, hydrogen, and oxygen, they differ in respect of the proportions between the combined carbon and hydrogen. Asking you to bear in mind how the equimolecular mixture of ethane and oxygen on explosion gave rise to a black cloud of carbon and a considerable formation of water, I will now fire the other two mixtures. You will observe that in neither case has there been any deposition of carbon, and an inspection of the cold bulbs will show that little or no steam formation has occurred. In fact the hydrocarbon has been burnt to carbonic oxide and hydrogen, leaving the hydrogen absolutely untouched by the oxygen.

[1] Jour. Chem. Soc., **85,** 694 (1904).
[2] Proc. Roy. Inst., **19,** 82 (1908).

"These experiments have an important bearing on the chemistry of flames. Hydrogen is usually considered as one of the most combustible of gases, but here we see it pushed to one side by the all-powerful hydrocarbon, as though it were so much inert nitrogen. This at once raises another question which has lately been occupying my attention. Ever since Davy's experiments on flame, the combustibility of hydrogen has been considered to be superior to that of methane; this, however, cannot be true in regard to slow combustion, since it can be easily proved that between 300° and 400° methane is oxidized at a far faster rate than hydrogen. Nevertheless I have recently observed facts which incline me to think that it may possibly be true in regard to flames. If further investigation confirms this opinion, it will be necessary to enquire into the cause of the peculiar relative inertness and stability of methane as compared with other gaseous hydrocarbons when subjected to the action of oxygen at high temperatures."

Later work showed that even at high temperatures methane is burned preferentially.[1] "The possibility of deducing from our bomb experiments a direct comparison between the relative affinities of methane and hydrogen in explosions arose from the fact that the primary oxidation of methane involves a direct transition from $CH_4 + O_2$ to $CH_2(OH)_2$, which latter breaks up ultimately into $CO + H_2 + H_2O$ without any deposition of carbon. Whence it follows that if mixtures, $CH_4 + O_2 + xH_2$, be exploded, the division of the oxygen between the methane and hydrogen during the extremely short period of actual combustion (i. e., direct oxidation) may be deduced from the proportion of the original methane found intact in the final products, provided always that there is no separation of carbon, which in fact is never observed in such circumstances.

"The experimental method consisted therefore in exploding a series of mixtures, $CH_4 + O_2 + xH_2$, in which the hydrocarbon and oxygen were initially present in as nearly as

[1] Bone: Phil. Trans., **215**, 298 (1915).

possible equimolecular proportions, but in which x (the volume ratio of H_2 to CH_4) was varied between 2 and 3, and determining from the percentage of the original methane remaining intact in each case (1) the oxygen distribution when $x = 2$ and (2) the influence upon such distribution of successive equal increments of x up to 8. And in order to determine the possible influence of the walls of the explosion vessel upon the results, parallel series of experiments were carried out in each of the two bombs, A (capacity about 103 cc) and B (capacity about 275 cc). In each case the mixture exploded with a distinctly audible sound, which diminished in intensity as the proportion x of hydrogen increased, until with the mixture $CH_4 + O_2 + 8H_2$ only a faint puff was heard. In no case was there any separation of carbon. The mean results of the experiments, so far as the distribution of oxygen between methane and hydrogen is concerned, are summarized in Table III.

TABLE III

Explosion of mixtures $CH_4 + O_2 + xH_2$

$x =$	2	4	6	8
Bomb A	%	%	%	%
O_2 to CH_4	95.3	81.0	54.9	31.4
O_2 to H_2	4.7	19.0	45 1	68.6
Bomb B				
O_2 to CH_4	97.1	91.0	72 6	—
O_2 to H_2	2.9	9.0	27.4	—

"It is at once evident from the results with the mixture $CH_4 + O_2 + 2H_2$ that *the affinity of methane is at least twenty to thirty times greater than that of hydrogen for oxygen in explosions.* The actual distribution of oxygen when a particular mixture is exploded is undoubtedly influenced to some extent by the walls of the containing vessel but not by the absolute initial pressure. The influence of the containing walls would presumably disappear after a certain limiting ratio of area to volume is attained, and, had the resources at our disposal permitted, it would have been interesting to have made

further experiments with a still larger bomb than B. An examination of the summarized results in Table III leads to the important conclusion that *the influence of successive increases in x, the volume ratio of H_2 to CH_4 in the mixture exploded, upon the actual oxygen distribution for a given vessel is proportional to x^2.* This can hardly mean other than that in explosion flames hydrogen is directly burned to steam as the result of trimolecular impacts, $2H_2 + O_2 = 2H_2$.

"The success of the experiments described in the preceding section led us to make a similar attempt to determine the division of oxygen between methane and carbon monoxide when mixtures of the general composition $CH_4 + O_2 + xCO$ are exploded under pressure. In this we were not completely successful, owing to a slight separation of carbon in the explosions whenever x exceeded 3.0 or thereabouts. Provided, however, the x did not exceed this limit, no carbon was deposited during the explosion, and such experiments may be given in detail as quite reliable so far as the question of the oxygen distribution between the two inflammable constituents is concerned." When the mixture $CH_4 + O_2 + 3CO$ was exploded in bomb A, 91–92 percent of the oxygen reacted with the methane and only 8–9 percent with the carbon monoxide. With the mixture $CH_4 + O_2 + 6CO$ in bomb A about 20 percent of the oxygen reacted with the carbon monoxide and only 16–17 percent with the same mixture in bomb B. These values of 20 percent in bomb A and 17 percent in bomb B for carbon monoxide correspond with 45.1 percent and 27.4 percent for hydrogen. When the mixture $CH_4 + O_2 + 2CO$ was exploded in bomb B 4.7 percent oxygen reacted with the carbon monoxide as against 2.9 percent reacting with the hydrogen in the corresponding experiment of Table III. At low concentrations ($x = 2$) a little more carbon monoxide is oxidized than hydrogen but it is very much the other way when $x = 6$.

"It is important to compare the results obtained with the foregoing $CH_4 + O_2 + xCO$ mixtures not only among themselves, but also with the results of the corresponding experi-

ments with $CH_4 + O_2 + xH_2$ mixtures. In the first place, it is evident that the affinities of either hydrogen or carbon monoxide are greatly inferior to that of methane for oxygen in explosion flames; thus it may be inferred from the experiments with $CH_4 + O_2 + 2H_2$ that the ratio of the affinities [really reaction velocities] $CH_4 : H_2$ is of the order 20 or 30 to 1 at least, and probably higher if the influence of the walls of the containing vessel could be eliminated. Owing to the uncertainty of our knowledge as to the precise mechanism of the combustion of carbon monoxide in explosions, that is to say, as to the extent and character of the intermediary action of steam, it is perhaps difficult to assign, even approximately, any numerical relation between the affinities of methane and carbon monoxide for oxygen in flames. Nevertheless, it may be pointed out, without laying undue stress on the fact, that when the mixtures, initially containing methane, hydrogen, or carbon monoxide, and oxygen in stoichiometrical proportions (i. e., $CH_4 + O_2 + 2H_2$ and $CH_4 + O_2 + 2CO$) were exploded under similar conditions in bomb B, the carbon monoxide was apparently more effective than hydrogen in pulling away oxygen from the predominating affinity of the hydrocarbon. [The reverse is true if one starts with $CH_4 + O_2$ and $6H_2$ or $6CO$.] From the theoretical standpoint it would probably be well worth while to undertake a further extended study of the matter in larger explosion vessels than we have employed, although it would be both a costly and a laborious enterprise.

"Whereas, in the case of hydrogen, the influence of successive increments in x, the volume ratio of the other combustible constituent to methane in the mixture exploded, upon the actual oxygen distribution is proportional to x^2 in the case of carbon monoxide, it is more nearly proportional to x. This points to some fundamental difference between the modes of combustion of the two gases in flames; thus whilst the evidence is strongly in favor of the supposition that hydrogen is burnt directly to steam as the result of trimolecular collisions $2H_2 + O_2 = 2H_2O$, the results with mixtures $CH_4 + O_2 + CO$ seem to require some different supposition, such, for instance, as an intermediary action of steam."

From the experiments of Henry, Landolt, and Bone, we see that hydrogen burns before methane at low temperatures in contact with platinum and at high temperatures when the gases are drawn off through a platinum tube. We see also that methane burns before hydrogen at moderate temperatures in borosilicate glass bulbs and also when the gases are fired by an electric spark. It is quite clear that a surface phenomenon is an important factor in changing the results. In Henry's experiments the platinum is unquestionably the cause of the preferential burning of the hydrogen and it seems probable that this is also true for Landolt's experiments. The existence of the water-gas equilibrium with hydrogen as one of the constituents is fairly strong evidence that hydrogen is more stable than methane. Bone's results may therefore be considered as approaching at high temperatures the results due to free burning away from a surface. This is the more probable because he always finds a greater relative oxidation of methane in the larger bomb where the ratio of surface to volume is less. The existence of a surface is also shown by Bone's observation that about 80 percent combustion of hydrogen occurs when the mixture $CH_4 + O_2 + 2H_2$ is passed over chamotte[1] at $500°$. I do not know enough about the adsorbing properties of chamotte to know just why it acts as it does; but this is a very striking reversal.

Since we can get almost complete preferential burning either of hydrogen or methane at moderate temperatures depending on the nature of the surface, it is probable that a more extended study of different surfaces would give us all the intermediate values for the distribution of oxygen between methane and hydrogen just as Sabatier and Mailhe[2] have found all sorts of gradations between the reactions $CH_3CH_2-OH = C_2H_4 + H_2O$ and $CH_3CH_2OH = CH_3CHO + H_2$ when alcohol is passed over different heated metals or oxides. While I have not been able to find any definite studies along

[1] Bone: Ber. deutsch. chem. Ges., 36, 12 (1913).
[2] Ann. Chim. Phys., [8] 20, 341 (1910).

this line, there are some indications that special results might be obtained with special solids.

Calvert[1] showed that oxygen adsorbed by boxwood charcoal oxidizes ethylene to carbon dioxide and water at ordinary temperatures. This is not surprising because charcoal adsorbs ethylene strongly. Since charcoal has little or no effect in causing hydrogen and oxygen to combine,[2] it is probable that we should get a preferential burning of ethylene in case a mixture of ethylene, hydrogen, and oxygen were brought in contact with charcoal. While this experiment seems not to have been tried, we do know that charcoal does seem to promote oxidation of carbon compounds.

In the form of wood ashes charcoal is often used in outhouses and elsewhere to eliminate unpleasant odors. The charcoal first adsorbs the odoriferous substances and then accelerates their oxidation, by oxygen which is adsorbed from the air. This dual function of the charcoal was pointed out clearly by Stenhouse[3] in 1854. "The powerful effects of freshly burned charcoal, especially when coarsely powdered, in absorbing gases and vapors, have long been known. Hence the limited extent to which charcoal has occasionally been employed to sweeten fetid water, and animal substances in the incipient stages of putrefaction. Sufficient attention has not, I think, however, been bestowed hitherto upon a second and still more important effect which charcoal exerts upon those complex products of decomposition; viz., that of oxidizing them rapidly, and resolving them rapidly into the simplest combinations they are capable of forming. . . .

"My attention was particularly drawn to the importance of charcoal as a disinfecting agent by my friend, John Turnbull, Esq., of Glasgow, the well-known extensive chemical manufacturer. About nine months ago Mr. Turnbull placed the bodies of two dogs in a wooden box, on a layer of charcoal powder of a few inches in depth, and covered them with a

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[1] Jour. Chem. Soc., **20**, 293 (1867).
[2] See, however, Craig: Chem. News, **90**, 109 (1904).
[3] Pharm. Jour., **13**, 454 (1854).

quantity of the same material. Though the box was quite
open and was kept in his laboratory, no effluvia were ever
perceptible. On examining the bodies of the animals at the
end of six months, scarcely anything remained of them except
their bones. Mr. Turnbull sent me a portion of the charcoal
powder which had been most closely in contact with the
bodies of the dogs. I submitted it for examination to one
of my pupils, Mr. Turner, who found it contained com-
paratively little ammonia, not a trace of sulphuretted hydrogen,
and very appreciable quantities of nitric and sulphuric acid,
with acid phosphate of lime. About three months ago, Mr.
Turner subsequently buried two rats in about two inches of
charcoal powder, and a few days afterward the body of a full
grown cat was treated similarly. Though the bodies of these
animals are now in a highly putrid state, not the slightest odor
is perceptible in the laboratory.

"From this short statement of facts, the utility of char-
coal powder, as a means of preventing noxious effluvia from
churchyards and from dead bodies in other situations, such
as on board ship, is sufficiently evident. Covering a church-
yard to the depth of from two to three inches with coarsely
powdered charcoal would effectually prevent any putrid
exhalations ever finding their way into the atmosphere.
Charcoal powder also greatly favors the rapid decomposition
of the dead bodies with which it is in contact, so that in the
course of six or eight months little is left except the bones.

"In the modern systems of chemistry, such, for instance,
as the last edition of 'Turner's Elements,' charcoal is de-
scribed as possessing antiseptic properties, while the very
reverse is the fact. Common salt, nitre, corrosive sublimate,
arsenious acid, alcohol, camphor, creosote, and most essential
oils, are certainly antiseptic substances, and, therefore, retard
the decay of animal and vegetable matters. Charcoal, on the
contrary, as we have just seen, greatly facilitates the oxida-
tion—and consequently the decomposition—of any organic
substances with which it is in contact. It is, therefore, the
very opposite of an antiseptic."

Shenstone invented a respirator[1] filled with powdered wood charcoal "to destroy any miasmata or infectious particles present in the air in the case of fever and cholera hospitals, and of districts infected with ague, yellow fever, and similar diseases. The object in view is, by filtering the air through such a porous substance as wood charcoal, to intercept the miasmata which may have got mixed with it. These, I think, cannot fail to be absorbed by the pores of the charcoal, where they will be rapidly oxidized and destroyed by the condensed oxygen with which they will be brought into the most intimate contact. The probability of this expectation being realized is greatly strengthened by the results of repeated trials with the respirator on certain noxious and offensive gases, such as ammonia, sulphuretted hydrogen, hydrosulphate of ammonia, and chlorine. I have found that air, strongly impregnated with these gases, and which could not be respired for any length of time under ordinary circumstances, may be breathed with impunity when the charcoal respirator is worn, the odor of these gases being rendered almost, if not altogether, imperceptible. Any other highly porous substance, such for instance as spongy platinum, or pounded pumice-stone, might probably be found to answer perfectly well for filling the respirator, but I have selected charcoal as the cheapest and most easily available material.

"While the filtration of water through charcoal powder and other porous substances has been advantageously practised for many centuries, the object in view being to deprive the water of numerous impurities diffused through it, which produce injurious effect on the animal economy, it is certainly somewhat remarkable that the very obvious application of a similar proceeding to the lighter fluid in which we live, viz., air, which not infrequently contains even more noxious impurities floating in it than are usually present in water, should have been overlooked so unaccountably up to the present time."

The combined deodorizing and oxidizing action of char-

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[1] The first of the modern gas masks.

coal accounts for a fact which has puzzled some campers, that there is no apparent relation between the amount of wood ashes needed and the number of people using an out-house.

In this case there may well be a special catalytic action because Shenstone[1] has pointed out that "the absorbent power of charcoal is comparatively much greater than its capacity for inducing chemical combination. In this respect charcoal presents a remarkable contrast to spongy platinum, which, though inferior as an absorbent for some gaseous substances—such, for instance, as ammonia, of which spongy platinum absorbs only 30 volumes, while charcoal absorbs 90—is, nevertheless, immensely more effective, both as an oxidizer, and as a promoter of chemical combination generally. As it is desirable for some purposes, while retaining the absorbent power of charcoal unimpaired, to increase its oxidating influences, it struck me that this important object might be easily effected by combining the charcoal with minutely divided platinum. In this way, a combination is produced to which I have given the name of platinized charcoal, which possesses the good properties of both of its constituents. In order to platinize charcoal, nothing more is necessary than to boil the charcoal, either in coarse powder or in large pieces, in a solution of bichloride of platinum, and when the charcoal has become thoroughly impregnated with the platinum, which seldom requires more than ten minutes or a quarter of an hour, to heat it to redness in a closed vessel—a capacious platinum crucible being very well adapted for this purpose. When 150 grains of charcoal were impregnated with nine grains of platinum by the process just described, the charcoal was found to have undergone no change in its external appearance, though its properties had been altered very essentially. When a few grains of this platinized charcoal were passed up into a mixture of dry oxygen and hydrogen in the proportions to form water, over mercury, the two gases combined rapidly in the course of a few minutes, precisely

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[1] Jour. Chem. Soc., 8, 105 (1856).

in the same way as when a clay ball of spongy platinum is employed. When, however, a fragment of charcoal containing a considerably larger proportion of platinum was passed up into a similar mixture, the gases combined instantly with explosive violence, just as if platinum black had been used. If pieces of cold platinized charcoal are held in a jet of hydrogen, they speedily become incandescent, and inflame the gas. Platinized charcoal, when slightly warmed, likewise rapidly becomes incandescent in a current of coal gas, but the jet of gas is not inflamed, owing to the very high temperature, a white heat, which is required for this purpose. In the vapor of alcohol or wood-spirit, platinized charcoal becomes red-hot and continues so till the supply of vapor is exhausted. In the course of a few hours, spirits of wine, in contact with platinized charcoal and air, are converted into vinegar. I find that 2 percent of platinum is sufficient to platinize charcoal for most purposes. Charcoal containing this small amount of platinum causes a mixture of oxygen and hydrogen to combine perfectly in about a quarter of an hour, and this is the strength of platinized charcoal that seems best adapted for charcoal disinfectant respirators. Charcoal containing 1 percent of platinum causes a mixture of oxygen and hydrogen to combine in about two hours; and charcoal containing the extremely small quantity of $1/4$ percent platinum produces the same effect in from 6 to 8 hours."

Of course it is not certain that the effect of charcoal on the dead dogs was exclusively an oxidizing action due to oxygen adsorbed by the charcoal. Some part of the result may very well have been due to micro-organisms which Stenhouse could not be expected to know about.

It is interesting to note that Bone's experiments on surface combustion led him to the conclusion that adsorption played an important part in the phenomenon. Bone[1] began by a study of the combination of hydrogen and oxygen in contact with hot surfaces of porcelain, magnesia, silver, gold, platinum, nickel, calcined spathic iron ore (containing 79.0

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[1] Phil. Trans., 206A, 1 (1906).

percent ferric oxide and 14.5 percent manganous oxide), nickelous oxide, and copper oxide. With each of these surfaces the rate is proportional to the pressure of the dry gas when electrolytic gas is used, is approximately proportional to the partial pressure of hydrogen when either gas is present in excess, and is increased by a previous treatment with hydrogen. In the case of porcelain Bone decides that "porous porcelain occludes or condenses both hydrogen and oxygen at rates which depend to some extent upon the physical condition and past history of the surface. In general, however, whereas in the case of oxygen the process is extremely rapid and the surface layer is soon saturated, the occlusion of hydrogen is slower and the limit of saturation much higher. Combination between the occluded gases occurs at a rate either comparable with, or somewhat faster than, the rate at which the film of occluded oxygen is renewed, but considerably faster than the rate of occlusion of hydrogen."

The behavior of magnesium, "together with the fact that the material occludes hydrogen but not oxygen at red heat, shows that the catalytic action must be referred to the power of occluding hydrogen." The catalytic action of the four metals examined is due primarily "to an association of the surface with hydrogen—in the case of silver probably to the formation of an unstable hydride, in the other three cases to an occlusion of the gas. The evidence in favor of the 'occlusion' theory is particularly strong in the case of nickel, where the 'normal' condition of activity can be reduced almost to the vanishing point by prolonged exhaustion at a comparatively low temperature. Moreover, the subsequent recovery of activity can be demonstrated by circulating successive charges of electrolytic gas over the surface under conditions which entirely preclude any chemical action of either of the reacting gases on the metal." "Considering the results obtained with the three different reducible oxides as a whole, they seem to be quite incompatible with any purely chemical explanation of the catalytic process. In the case of copper oxide it would appear to involve the condensation of a film of 'active' oxygen

on the surface, and that this film actually protects the catalyz-
ing oxide from the attacks of the hydrogen, which would
otherwise reduce it energetically. At low pressures the film
becomes too attenuated to ensure complete protection, and in
consequence, the formation of steam is accelerated by reason
of hydrogen penetrating through onto the oxide and reducing
it. In conformity with this idea, the rate of steam formation
when the gases are not present in combining ratios was found
to be proportional to the partial pressure of the oxygen.

"In the cases of the other reducible oxides examined, the
fact that the gases combined at moderate temperatures,
without permanently altering the surface, and at rates always
far in excess of the rates at which either the surface was re-
duced by hydrogen, or the reduced surface reoxidized, does
not harmonize with the purely chemical theory. It is difficult
to resist the conclusion that in these cases also the catalytic
action is due primarily to a physical condensation of one or
other of the reacting gases at the surface. Since the rate of
combination was always proportional to the partial pressure
of the hydrogen in all experiments where the gases were not
present in combining ratios, it would appear to be the hydrogen
which is condensed and so rendered active."

The fact that the catalytic combustion depends on an
intimate contact of the reacting gases with the surface is shown
by the appearance of a piece of silver gauze before and after
it had acted as catalytic agent for hydrogen and oxygen at
400°. The wires were originally very smooth but after using
they became quite rough. Bone[1] points out that at very
high temperatures the specific nature of the solid seems to be
relatively unimportant. At such temperatures one would get
practically no displacement of equilibrium by the catalytic
agent because the reaction in the gas phase takes place so
rapidly that the final equilibrium is that of the gas phase and
not that of the catalytic agent.

[1] Ber. deutsch. chem. Ges., 46, 14 (1913).

The general conclusions to be drawn from this paper are:

1. At low temperatures the nature of the catalytic agent may determine which of two combustible gases will burn the more rapidly.

2. As might be expected hydrogen burns more readily than methane or ethylene in presence of platinum.

3. From Landolt's experiments the same seems to be true in the flame provided a platinum tube is inserted; but these experiments should be repeated.

4. In presence of copper oxide at 250° all the hydrogen in a mixture of hydrogen and methane can be burned without any of the methane being decomposed.

5. In presence of chamotte at 500° hydrogen burns much more readily than methane. So little is known about the adsorption by chamotte that this result could not have been predicted.

6. In borosilicate glass bulbs at 300°–400° methane, ethane, ethylene, and acetylene are oxidized much more rapidly than hydrogen or carbon monoxide.

7. When mixtures of methane, oxygen, and hydrogen or carbon monoxide are exploded by an electric spark the methane burns much more rapidly than either the hydrogen or the carbon monoxide.

8. Depending on conditions either hydrogen or carbon monoxide will burn the more readily.

9. Since charcoal causes ethylene to be oxidized to carbon dioxide and water, and since charcoal has very little effect on a mixture of hydrogen and oxygen, it is probable that charcoal would cause preferential burning of ethylene in a mixture of ethylene and hydrogen.

10. By suitable selection of the catalytic agent it should be possible to get all intermediate stages from complete burning of methane to complete burning of hydrogen.

11. Since relatively more methane was burned in the explosion experiments the larger the bulb, it seems probable

STUDIES IN CONTACT CATALYSIS

BY CARL J. ENGELDER

DECOMPOSITION OF ETHYL ALCOHOL

Introduction

A great deal of work has been done on catalysis in hetero-geneous systems especially in regard to increasing the reaction velocity between gases by contact with solid catalytic agents. The phenomenon is called contact catalysis, and takes place at the surface of the oxide or finely divided metal. While catalytic action in both homogeneous and heterogeneous systems can be explained in many instances by the formation of intermediate compounds between the reacting substances and the catalyst, this theory does not explain all cases of in-creased reaction velocity. The catalytic decomposition of hydrogen peroxide is explained by Haber by the alternate oxidation and reduction of the metal according to the equa-tions

$$y\mathrm{H_2O_2} + n\mathrm{Pt} = \mathrm{Pt}_n\mathrm{O}_y + y\mathrm{H_2O}$$
$$\mathrm{Pt}_n\mathrm{O}_y + y\mathrm{H_2O_2} = n\mathrm{Pt} + y\mathrm{H_2O} + y\mathrm{O_2}.$$
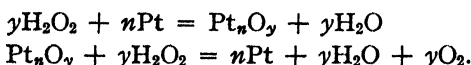
Yet the only case where the metallic oxide has been isolated is that of mercury, $\mathrm{HgO_2}$, and there seems to be no evidence for the existence of platinum oxides in this catalysis. More-over, Wöhler[1] found that PtO and $\mathrm{PtO_2}$ were actually less active than metallic platinum in the contact sulphuric acid process. The existence of a platinum hydride has not been definitely proven.

We must therefore look to adsorption at the interface for an explanation of increased reaction velocity. Since surface adsorption is a universal phenomenon and since gaseous reactions are catalyzed by the increased concentration of the reacting substances in the surface layer, it is natural to assume that all reactions may be catalyzed by the walls of the con-taining vessels. This has been shown by Bodenstein[2] to be

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[1] Ber. deutsch. chem. Ges., **39**, 3578 (1906); **42**, 3326 (1909).
[2] Zeit. phys. Chem. (1903–1907).

true in many cases. Van't Hoff,[1] furthermore, showed that the rate of polymerization of cyanic acid depended on the superficial area of the walls of the vessel. Bodenstein[2] says that a "full explanation of all the phenomena [of heterogeneous catalysis of gas reactions] is given by the assumption that the further reaction process is retarded by the product of the reaction in those cases in which this product is more condensable and more easily adsorbed than the initial reacting substances themselves. There is, in fact, an adsorption layer, or in certain cases, an ordinary liquid or solid skin formed upon the catalyst through which the reacting substances must pass by diffusion in order to come into contact with the catalyst, where they react with practically instantaneous velocity."

Bodenstein has overlooked the fact that the strong adsorption of the reaction products may be an important factor in causing the reaction to take place at all. If a substance may react in two ways, that reaction will predominate for which the reaction products are most strongly adsorbed by the catalytic agent. The theory of this has been explained in detail by Professor Bancroft[3] and this paper furnishes experimental confirmation of it.

There are two ways in which ethyl alcohol decomposes catalytically. The first is a dehydration, resulting in the production of ethylene. The second is one of dehydrogenation in which the alcohol breaks up into hydrogen and acetaldehyde. These reactions are represented by the following equations:

$$CH_3CH_2OH \longrightarrow H_2O + CH_2 : CH_2$$
$$CH_3CH_2OH \longrightarrow H_2 + CH_3CHO$$
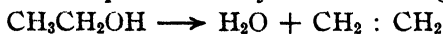
Sabatier and Mailhe[4] found that with thoria, ThO_2, at a temperature of 340°–350° the ethylene reaction took place exclusively. Alumina, Al_2O_3, at the same temperature acts practically as a dehydrating agent, the second reaction being almost negligible. With various other metallic oxides the two

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[1] "Études," 55 (1884).
[2] Zeit. phys. Chem., **60**, 61 (1907).
[3] Jour. Phys. Chem., **21**, 573 (1917).
[4] Sabatier and Mailhe: Ann. Chim. Phys., [8] **20**, 289 (1910).

reactions take place side by side. Finely divided metals, on the other hand, such as Cu, Ni, Co and some oxides, of which manganous oxide, MnO, is best, yield almost pure hydrogen and aldehyde. This latter reaction is complicated by the fact that at these temperatures the aldehyde is partially decomposed into methane and carbon monoxide. The catalysts studied by Sabatier and his co-workers have been arranged in a table, in the order of their function as dehydrating agents.

TABLE I[1]

Oxide (prepared below 350°)	Vol gas per min.	100 cc contain	
		% C₂H₄	% H₂
ThO₂	31.0	100.0	traces
Al₂O₃	21.0	98.5	1.5
W₂O₃ (blue)	57.0	98.5	1.5
Cr₂O₃	4.2	91.0	9.0
SiO₂	0.9	84.0	16.0
TiO₂	7.0	63.0	37.0
BeO	1.0	45.0	55.0
ZrO₂	1.0	45.0	55.0
UO₂	14.0	24.0	76.0
Mo₂O₅ (blue)	5.0	23.0	77.0
Fe₂O₃	32.0	14.0	86.0
V₂O₃	14.0	9.0	91.0
ZnO	6.0	5.0	95.0
MnO₂	3.5	0	100.0
SnO	45.0	0	100.0
CdO	11.2	0	100.0
Mn₃O₄	12.0	0	100.0
MgO	traces	0	100.0
Cu	110.0	0	100.0
Ni	—	0	100.0

It was with the purpose of studying a displacement of the equilibrium in the catalytic decomposition of alcohol that the researches recorded in the following pages were undertaken. Alumina, as noted above, functions almost exclusively as a dehydrating catalyst. The question arises whether or not this

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[1] Sabatier and Mailhe: Ann. Chim. Phys., [8] **20**, 341 (1910).

specific property can be influenced by the addition of water to the reacting vapor phase, and thus the amount of water actually adsorbed from the alcohol molecule be reduced, resulting in a corresponding lower yield of ethylene in the gaseous mixture. There would thus be a displacement of the equilibrium with a relative increase in velocity of the aldehyde reaction. Catalysts such as silica and titania, since they yield greater amounts of hydrogen, ought to show this effect more markedly.

Frederiksen undertook a study of this problem using alumina as catalyst. His unpublished work shows that while the addition of water cut down the velocity it did not apparently alter the ethylene content. This, it was shown later, was due to the disturbing effect of aldehyde vapors, a difficulty which was later removed.

Apparatus

The general plan of procedure was to pass the heated vapors over the hot catalyst and to collect the resulting gaseous and liquid products in suitable collecting devices. A sketch of the apparatus used is shown in the accompanying diagram. The alcohol or aqueous solution was measured
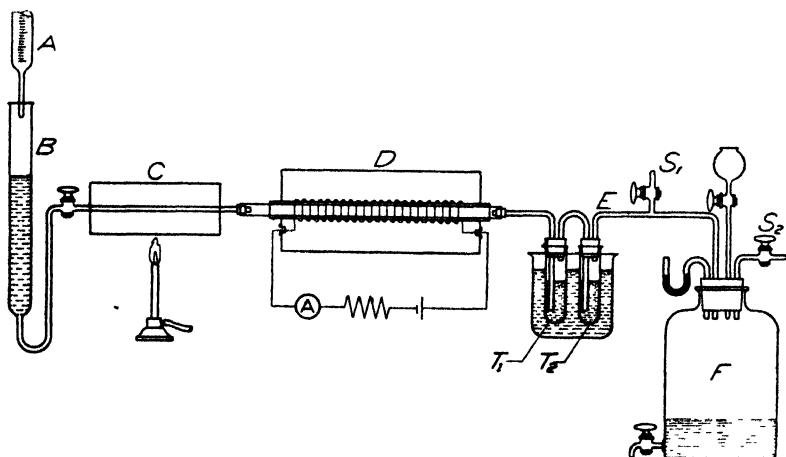
from the burette A into the regulator B which served to keep the rate of flow uniform. Adjustment could easily be

made by means of the capillary stopcock. The capillary tube from the regulator passed through the asbestos jacket C which was maintained at a constant temperature by means of the burner underneath. The heated vapors were led through the furnace, in which were placed two 10 cm porcelain boats containing the powdered oxide. The furnace consisted of a nichrome-wound alundum tube surrounded by plumber's packing and contained in a sheet iron shell. Fitting snugly within the alundum tube was a porcelain tube 1.5 cm in diameter and 50 cm long. The temperature of the furnace could be well controlled by adjustment of the lamp bank resistance. A 100 volt current was used.

Two large test tubes immersed in freezing mixture were inserted in the chain. One, T_1, served to collect the liquid products of the decomposition and the other, T_2, contained strong alkali to free the gases from aldehyde vapors. The sampling tube S_1 was used when a continuous sample of the gas was desired.

The gases passed on into the container F which was provided with a manometer, sampling capillary, S_2, outlet tube and separatory funnel for adding the confining liquid. Saturated salt solution, in which the gases are only slightly soluble, was used in the gas holder. The rate of evolution of the gas could be measured by measuring the volume of liquid displaced in the bottle.

Great care was taken to maintain conditions as uniform as possible. The rate of adding the vapors was regulated by the stopcock in the capillary. The furnace was heated for several hours before making a run to ensure constant temperature and temperatures were determined by a pyrometer inserted in the furnace. Current was read off the ammeter A.

The catalysts, in general, were prepared by precipitating the hydroxide in dilute solution with ammonium hydroxide. The gelatinous or flocculent precipitates were washed thoroughly, filtered, dried over phosphorus pentoxide for about a day and then heated in an air oven to not over 250°.

The dried solid was powdered in an agate mortar to a 200-mesh fineness. In each experiment, about 0.5 g of the oxide was used in the two combustion boats.

Analysis of the Gas Mixtures

The methods used in analyzing the gas mixtures are here given. The sample, withdrawn either directly from the apparatus or from the gas container, was measured out in a water-jacketed Hempel burette containing mercury as the confining liquid. The various constituents contained in the mixtures were determined as follows in the order given:

1. *Carbon Dioxide*—This was absorbed in 1 : 1 KOH contained in a Hempel single pipette. The pipette contained rolls of iron wire gauze to give a greater absorption surface.

2. *Ethylene*—In the earlier part of the work fuming sulphuric acid was used for determining ethylene. A three-minute passage of the gas back and forth through the acid, with a subsequent one-minute contact in the KOH pipette to remove SO_3 fumes usually sufficed for the absorption of all ethylene. Since, however, fuming sulphuric acid is known[1] to absorb the paraffine hydrocarbons to some extent, a 1 percent bromine solution was substituted for the acid to remove the ethylene. Bromine fumes were removed with KOH as above.

3. *Oxygen*—Alkaline pyrogallol prepared by the method of Anderson,[2] i. e., dissolving 15 g of pyrogallol in 100 cc of a solution of potassium hydroxide of specific gravity 1.55, removed all the oxygen with one-minute shaking.

4. *Carbon Monoxide*—The reagent for CO was ammoniacal cuprous chloride. This was made by adding 25 g of CuCl to 100 cc of strong NH_4OH to which had previously been added 20 g of NH_4Cl. After three-minute shaking in a double pipette, the ammonia fumes given off by the reagent were removed by passing the gas into a pipette containing 5 percent sulphuric acid.

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[1] Anderson and Engelder: Jour. Ind. Eng. Chem., **6**, 989 (1914).
[2] Anderson: Ibid., **7**, 587 (1915).

5. *Hydrogen*—This gas was determined by fractional combustion over copper oxide heated to $250°$-$270°$ C.[1] The contraction in volume gives directly the percentage of hydrogen. Before admitting the gas the air contained in the copper oxide tube must be displaced with nitrogen and a measured volume of nitrogen must be passed through the tube at the end of the determination, to sweep out all the hydrocarbon residue for the subsequent analysis.

6. *Methane and Ethane*—These gases were burned with a measured volume of oxygen in a Dennis combustion pipette. From the contraction in the volume observed after the combustion and the carbon dioxide formed, the percentages of methane and ethane, or methane and hydrogen can be calculated. The formulas for the former mixture are:

$$C_2H_6 = \frac{4CO_2 - 2TC}{3}$$
$$CH_4 = CO_2 - 2C_2H_6$$

and for hydrogen and methane:

$$H_2 = \frac{2}{3}(TC - 2CO_2)$$
$$CH_4 = CO_2$$

where TC represents the total contraction observed after combustion.

Alumina as Catalyst

Alumina was shown by Grigorieff[2] and by Sabatier and Mailhe[3] to be a very powerful dehydrating agent, its action upon ethyl alcohol yielding water and almost pure ethylene. The activity of the alumina depended greatly upon the conditions of its preparation; that made by precipitating the hydroxide from aluminum nitrate and drying at $300°$ C yields the best catalyst.

In the following experiments on Al_2O_3 as catalyst, the oxide was prepared according to the above method. 50 g. of $Al(NO_3)_3$ were dissolved in 2 liters of hot, distilled water, the solution divided into 5 parts, each diluted to about one

[1] Dennis: "Gas Analysis."

[2] Grigorieff: Bull. Soc. chim. Paris, [3] 26, 612 (1902).

[3] Sabatier and Mailhe: Ann. Chim. Phys., [8] 20, 298 (1910).

liter and 1 : 1 NH$_4$OH added to each portion until precipitation was complete. Washing by decantation six times, filtering and washing on the filter several times was considered sufficient to remove all salts. After drying over phosphorus pentoxide in a desiccator for 24 hours, the product was heated in an air oven at 240° C for several hours. It was then ground to pass a 200-mesh sieve.

The catalyst prepared in this way proved to be a very good product. After several preliminary runs with alcohol, the oxide being heated to about 500° C, its action was studied in more detail in the following experiments. Two small combustion boats were filled with the oxide and placed in the furnace in each case. The temperature was indicated on a pyrometer inserted in the furnace. Readings of the volume of gas evolved and the cubic centimeters of alcohol admitted were made every 15 minutes. In most cases the runs were of 2 hours' duration. In one experiment, however, made to determine the duration of activity of alumina, the time was extended over 5 hours; the catalyst showed a slight decrease in activity at the end of five hours probably due to agglomeration of the oxide particles.

The table below is typical of the results obtained in these experiments.

TABLE II

Absolute alcohol over Al$_2$O$_3$
Temperature of furnace = 490° C
Readings taken every 15 minutes

	First hour			
cc gas evolved	960	1000	1010	1020
cc total alcohol	2.8	5.65	8.3	11.0
cc alcohol	2.8	2.85	2.65	2.7
cc gas per cc alcohol	342	351	381	378
cc gas per minute	64	66	67	68
	Second hour			
cc gas evolved	1000	920	1000	910
cc total alcohol	13.9	16.5	20 5	23 2
cc alcohol	2.9	2.6	4.0	2 65
cc gas per cc alcohol	344	354	247	343
cc gas per minute	66	61	66	60

The gas from this experiment, calculated to an air-free basis, was 98.0 percent ethylene. The yield, obtained by reducing the gas volume to standard conditions and computing for C_2H_4, was 79 percent.

The effect of water vapor in cutting down the rate of reaction is shown in the following table. The rate of evolution per cubic centimeter of alcohol, as well as per minute over one-hour intervals, is tabulated as shown. The rate of admitting alcohol was kept as uniform as possible, about 10 cc alcohol from the regulator being added per hour. To maintain this alcohol rate for the aqueous mixtures the 50 percent solution has to be added twice as fast. That the resulting decrease in gaseous products did not occur as a result of increasing the rate of feeding was proven by a second experiment in which it was shown that the rate of admitting the alcohol did not materially affect the percentage yield. It is plausible in accordance with our theory of adsorption to account for the decreased activity on the basis of saturation of the contact surface with water vapor and hence a decreased power to take up more of the alcohol vapor.

TABLE III
Hourly averages for Al_2O_3
Temperature of furnace 490° C

Experiment	First hour				
	Total gas	Total alcohol	Gas per cc alcohol	Gas per minute	% C_2H_4
1—Absolute alcohol	4210	10.2	412	70.1	—
2—Absolute alcohol	3817	9.95	383	63.6	—
3—50% alcohol	2490	11.2	222	41.5	—
4—50% alcohol	3000	11.1	270	50.0	—
	Second hour				
1—Absolute alcohol	3987	9.5	419	66.4	98.2
2—Absolute alcohol	3995	10.15	393	66.5	98.4
3—50% alcohol	2185	7.6	287	36.4	97.5
4—50% alcohol	2650	9.95	266	44.1	97.6

The yields of ethylene, at different temperatures, for both absolute and aqueous alcohol, are herewith tabulated. The higher the temperature the greater the amount of decomposition.

TABLE IV

Decomposition by alcohol by Al_2O_3

Sample	Absolute alcohol				
	A_1	A_2	B_1	B_2	B_3
Temperature	490	490	490	420	380
Duration of run	2 hrs.	2 hrs.	2 hrs.	15 min.	15 min.
Total gas evolved	8197	7812	7820	1250	900
Total alcohol used	19.7	20.1	19 8	8.5	11.5
cc gas per cc alcohol	426	388	393	147	78.2
Percentage decomposition	94.5	78	79	33 5	81

Sample	Aqueous solution				
	A_3	A_4	B_4	B_5	B_6
Temperature	490	490	490	420	380
Duration of run	2 hrs.	2 hrs.	2 hrs.	15 min.	11 min.
Total gas evolved	4675	5330	5650	310	350
Total alcohol used	18 8	17.6	21 05	25.9	9.0
cc gas per cc alcohol	248	302	268	12.0	38.8
Percentage decomposition	56	69	61	2.7	8.9

The values, except for the aqueous run at 380° C, are consistent and show clearly the effect of water on the decomposition.

In studying the effect of the addition of water on the displacement of the equilibrium considerable difficulty was experienced, since the ethylene yield is so high that a relative increase in hydrogen, the other gaseous product, does not change the percentage composition of the gas mixture to any great extent, and the small residue of hydrogen is hard to determine accurately. After absorbing ethylene in 1 percent bromine water with subsequent removal of bromine vapors by KOH, the hydrogen was determined by combustion with

oxygen over mercury in a combustion pipette. Two sets of experiments, performed at 380° C and 420° C, respectively, are tabulated in the following table. "cc solution" denotes the total volume of liquid added during the run, whether absolute alcohol or the aqueous mixture. The condensate collected in the cooled receiver showed more aldehyde in the case of the aqueous solutions.

TABLE V

Displacement of equilibrium with Al_2O_3

	Absolute	Aqueous	Absolute	Aqueous
Temperature of run	420°	420°	380°	380°
Duration of run in minutes	15	15	15	11
cc gas evolved	1250	310	900	350
cc solution	8.5	51.8	11.5	18.0
cc alcohol	8.5	25.9	11.5	9.0
cc condensate collected	5.0	33.0	7.0	15.0
cc gas per cc alcohol	147	20.6	78.2	38 8
cc gas per minute	83.3	12.0	60.0	31.8
cc absorbed in bromine	97.2	93.2	98.0	92.4
cc absorbed pyrogallol	0.2	0.9	0.1	1.2
cc hydrogen by combustion	2.4	2.25	1.2	2.1
% C_2H_4	97.5	95.4	98.7	97.7
% H_2	2.5	4.6	1.3	2.3

The percentage of hydrogen is almost doubled when 50 percent alcohol is used, showing that the aldehyde reaction is greatly increased and the ethylene-water production cut down correspondingly.

Silica as Catalyst

Silica as a catalytic agent in the decomposition of alcohol shows extremely variable results depending upon the origin. Sabatier and Mailhe[1] found that finely powdered quartz as well as silica obtained from the decomposition of silicon fluoride, showed no appreciable action, whereas SiO_2 prepared from sodium silicate and hydrochloric acid exerted a mixed function upon primary alcohols, yielding, for ethyl alcohol, at 380° C, a gas mixture which contained 84 percent ethylene and 16 percent hydrogen.

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[1] Loc. cit., p. 325.

A sample of SiO_2 was prepared by precipitating the gelatinous silicic acid from Na_2SiO_3 by means of HCl, filtering, washing thoroughly and drying, first over phosphorus pentoxide and then in an air oven at 270° C. The action of this preparation was so slow, yielding, at a temperature of 490° C, about 300 cc gas during the three-hour run, that another sample of the catalyst was prepared.

This second sample was made by taking 50 cc syrupy sodium silicate and diluting this with 150 cc distilled water. This solution was then poured into 250 cc of 1 : 1 HCl. The limpid yellow solution of hydrated silica was heated nearly to boiling and the resulting jell broken up into fine masses, thoroughly washed, filtered, dried in a desiccator and air oven and then powdered to pass a 200-mesh sieve.

The silica thus prepared was a somewhat better catalyst than the first sample. The average of a number of runs with absolute alcohol yielded 5 cc gas per cubic centimeter of alcohol of which 82 percent was taken up in fuming sulphuric acid. The rate of evolution was about 4 cc per minute. Considerable air was mixed with the gas samples so no great reliance can be placed in the figures. The following table shows a typical run for alcohol, at 490° C, using about 0.5 g of oxide.

TABLE VI

Absolute alcohol over SiO_2
Temperature of furnace = 490° C

Time in minutes	cc gas evolved	cc alcohol used	cc gas per cc alcohol	cc gas per minute
15	65	14.5	4.5	4.3
30	55	7.6	7.2	3.7
45	68	8.7	7.8	4.5
60	57	8.9	6.4	3.8
75	54	8.4	6.4	3.6
90	57	9.6	5.9	3.8
105	58	8.6	6.7	3.9
120	57	9.8	5.8	3.8
135	57.5	9.2	6.2	3.8
150	64.5	8.9	7.2	4.3
165	54	8.1	6.6	3.6
180	55.5	8.8	6.3	3.7

The gas collected in the above run analyzed 84.2 percent C_2H_4.

Results were variable when water was added to the alcohol. In all cases, the rate of reaction was cut down nearly one-half, but in general, the composition of the gases did not differ materially from that obtained from pure alcohol. The gas, when recalculated to an air-free basis, and tabulated in the following table, did however show the looked-for decrease in ethylene content, 68.6 percent being absorbed in fuming sulphuric acid.

TABLE VII

Aqueous alcohol over SiO_2
Temperature of furnace = 490° C

	First hour			
cc gas evolved	75	30	28	34
cc solution added	9.7	11.0	9.7	9.3
cc alcohol added	4.8	5.5	4.8	4.6
cc gas per cc alcohol	15.6	6.0	5.8	7.4
cc gas per minute	5	2	1.9	2.3
	Second hour			
cc gas evolved	48	12	34	28
cc solution added	13.7	11.3	8.5	8.9
cc alcohol added	6.8	5.6	4.2	4.4
cc gas per cc alcohol	7.1	2.1	8.1	6.4
cc gas per minute	3.2	0.8	2.3	1.9

Thus, while absolute alcohol yields a gas mixture containing 84.2 percent ethylene the aqueous solution gives a mixture containing but 68.6 percent C_2H_4. Here, as in the case of Al_2O_3 the dehydration is cut down when water is added to the reacting mixture.

Zirconia as Catalyst

Among the catalysts showing a mixed action, zirconia was found to be very efficient. Sabatier and Mailhe[1] showed that ZrO_2 decomposed ethyl alcohol at 370°, giving 13 cc per

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[1] Ann. Chim. Phys., [8] 20, 334 (1910).

minute of gas which contained 45 percent ethylene and 55 percent hydrogen. Experiments were undertaken in connection with the present work to show a shifting of the equilibrium similar to that found with alumina and silica.

A sample of impure zirconium ore, finely ground, was first tried with no results. The same was true for ZrO_2 precipitated from the nitrate. A product, however, obtained by calcining the nitrate at a low heat, gave good results as shown in the table below.

TABLE VIII

Displacement of equilibrium with ZrO_2

	Absolute alcohol	50% alcohol
Temperature	380° C	380° C
Duration of run	25 min.	25 min.
cc solution added	24 2	46.4
cc alcohol	24 2	23.2
cc gas evolved	300	186
CO_2	0%	0%
C_2H_4	63.6	42 5
CO	2.1	0 0
H_2	31 5	49 0
CH_4	2 8	8 5
C_2H_6	0	0

The decrease in the percentage of ethylene as well as the increase in hydrogen shows, beyond question, that the first reaction is cut down and the second one accelerated by using aqueous alcohol.

Titania as Catalyst

Titania obtained by the dehydration of $Ti(OH)_4$ was found by Sabatier to be a very good catalyst in the decomposition of alcohol. At 320° C he found that ethyl alcohol is decomposed into almost pure ethylene. At higher temperatures, 360° C, the evolution of gas is more rapid, when both reactions set in, the composition of the gas being 64 percent C_2H_4 and 36 percent H_2. At 400° C the evolution is in the neighborhood of 31 cc per minute, and contains the two gases in the same proportion as above.

Considerable experimental work was done with TiO_2 which will be described in the following pages. The results in most cases are at variance with those obtained by Sabatier and will be discussed in order.

The first sample of TiO_2, Sample A, was obtained by calcining the sulphate $Ti(SO_4)_2$ directly in the furnace. After the evolution of SO_3 had ceased, a run was made at 490° C with absolute alcohol. The evolution of gas was quite rapid. It had a very pungent, disagreeable odor and filled the receiving bottle with white fumes. The odor was that of mercaptan. The formation of mercaptan from alcohol was studied by Sabatier[1] who found that when H_2S was led into the reacting chamber with alcohols in the presence of ThO_2, ZrO_2, Cr_2O_3 and other metallic oxides, high yields of mercaptan were obtained. In the above experiment the hydrogen reduced the SO_3, which was not entirely driven out, to H_2S, and this in presence of TiO_2 reacted to form C_2H_5SH.

The data for this run, which is typical of results obtained in further experiments, are given herewith.

TABLE IX
Absolute alcohol over TiO_2 (A)
Temperature of furnace 490° C

Time in minutes	cc gas evolved	cc alcohol added	cc gas per minute
15	735	7.1	49
30	420	2.8	25
45	365	3.8	24
60	330	4.4	22
75	290	3 1	19
90	230	5.0	15
105	225	2.8	15
120	223	3.1	15

There is a gradual falling off in the gas evolution with time, due to changes in the surface of the contact material. The gas contained 61.4 percent absorbable in $H_2S_2O_7$. No analysis was made of the unabsorbable residue.

[1] Sabatier: "Die Katalyse in der organischen Chemie," 179–181.

A second sample of TiO$_2$ was prepared by dissolving 5 g of Ti(SO$_4$)$_2$ in strong H$_2$SO$_4$, diluting to 2 liters and adding enough strong NH$_4$OH to precipitate the titanium as Ti(OH)$_4$. The flocculent precipitate was washed 8 times by decantation, filtered, washed, dried over P$_2$O$_5$ and then heated in an air oven at about 150° C for two hours. This product was designated as B. In the following series of experiments the procedure was the same in all runs. Several hours of preliminary heating were allowed to ensure thermal equilibrium of the furnace, the temperature being read off the pyrometer and controlled with the lamp bank resistance. The reaction was allowed to proceed long enough to sweep all air out of the apparatus before actual readings were taken. Runs with absolute, 50 percent, and 25 percent alcohol were made. The results are given in the accompanying table. The temperature was maintained at 490° C.

TABLE X

Sample	Absolute B$_1$	Absolute B$_2$	50 % B$_3$	50 % B$_4$	25 % B$_5$
Total gas evolved	2813	3265	1430	1219	644
Total alcohol	24.5	32.8	35 6	41.7	31 57
cc gas per cc alcohol	114	99	40 1	29 0	26 0
cc gas per minute	23.4	27.2	11 9	19.1	5 3
cc ethylene	81.9	86.2	64.2	62 4	47.4
cc oxygen	0 2	0 2	0 5	0 8	1 4
% C$_2$H$_4$	82 7	87 0	66.9	65.0	48 4
% unabsorbable	17 3	13 0	33 1	35 1	51.6

The data are averaged over two-hour intervals. Readings taken in the original experiments every 15 minutes show the rate of decomposition to slowly and gradually decrease with time. The olefine was absorbed in H$_2$S$_2$O$_7$ and the oxygen of the air with which the gases were always slightly contaminated by alkaline pyrogallol. The unabsorbable residue consists chiefly of hydrogen, but contains also ethane and small amounts of methane and carbon monoxide. The percentages are calculated to an air-free basis.

The duplicates for the several runs, it will be noted, agree quite closely.

In order to bring out the effect of adding water more strikingly the following table is given in which the average is taken.

TABLE XI

Runs	Absolute	50 %	25 %
cc gas evolved	3039	1324	644
cc solution added	28.65	77.0	126.28
cc alcohol used	28.65	38.5	31.57
cc gas per cc alcohol	107.4	34.6	26.0
cc gas per minute	25.3	11.0	5.3
% C_2H_4	84 8	65.9	48.4
% unabsorbable	15.1	34.0	51.6

By inspection of the above table it will be seen clearly that the addition of water has a great effect upon the decomposition of the alcohol. Not only is the rate of evolution cut down greatly but the amount of decomposition, or the yield of gas per cc alcohol is reduced. The greater change, however, occurs in the composition of the gas. While 100 percent alcohol gives a gas, 84.8 percent of which is absorbable in fuming sulphuric, the 50 percent water mixture yields 65.9 percent C_2H_4 and the 25 percent aqueous solution 48.4 percent C_2H_4. There is a corresponding increase in the unabsorbable residue, which consists, not only of H_2 but also C_2H_6 and small amounts of CH_4 and CO.

Further experiments were undertaken on the displacement of the equilibrium with TiO_2. A sample of TiO_2, prepared by precipitating the hydroxide from $TiCl_4$ instead of $Ti(SO_4)_2$ and subsequent washing, filtering and drying yielded, at 380° C, a gas which contained as an average of several runs 59 percent C_2H_4. Complete analyses were made of the gas given off in several runs with absolute and aqueous alcohol. The presence of ethane was not suspected until the gaseous residue after absorbing ethylene, oxygen, carbon monoxide and removing the hydrogen by combustion over CuO showed,

upon combustion, large amounts of carbon dioxide. Applying the combustion equation for C_2H_6 and CH_4, obtained by computing from the contraction observed and the carbon dioxide formed, it was found that the reaction between C_2H_4 and H_2 is greatly catalyzed by TiO_2 at the temperature of the experiment, yielding varying amounts of C_2H_6. The amounts of CH_4 formed were always small and corresponded in most cases to the CO present, both the gases re sulting from the breaking down of the aldehyde formed along with the hydrogen. Higher percentages of methane than those corresponding to CO can be accounted for on the basis of the reaction between carbon monoxide and H_2,

$$CO + 3H_2 = CH_4 + H_2O,$$
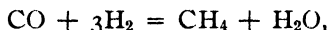
which reaction takes place to some extent.

The formation of C_2H_6 complicated the reaction to some extent, and in order to ascertain the total ethylene and hydrogen formed, a calculation must be made to obtain the ratio between C_2H_4 and H_2. Carbon monoxide occurs in very small quantities, so that a recalculation can be made on a carbon monoxide-methane as well as air-free basis. Since each volume of ethane represents one volume of ethylene and one of hydrogen, the total amount of C_2H_4 formed will be given by the sum of C_2H_4 and C_2H_6. Similarly, H_2 originally formed equals H_2 actually present plus the volume of C_2H_6 determined. Upon this basis then the ratios are found, as shown in the table.

Similar sets of values were obtained from a sample of TiO_2 (E) made from the sulphate. Both sets are shown below.

The ratio of ethylene to hydrogen agrees well in both sets, being greater for absolute than for aqueous alcohol. The two runs with absolute alcohol agree within the experimental limit even though the sample of catalyst is of different source, but in the case of the aqueous mixtures the ethane formation has taken place to a much greater extent with Sample E than with Sample D. In fact, the secondary re-

TABLE XII
Displacement of equilibrium with TiO₂
Temperature 380°

Experiment	Absolute (D₇)	50% (D₄)	Absolute (E₁)	50% (E₂)
C_2H_4	54	49.2	55	31
CO	0	0.6	2.7	0.0
H_2	8.4	30.1	8.1	5.3
CH_4	2.1	1.6	4.0	0
C_2H_6	36.0	16.4	30.2	63.6
C_2H_4	54.8	51.4	59.0	31.0
H_2	8.5	31.1	8.7	5.3
C_2H_6	45.2	17.1	32.3	63.6
% C_2H_4	66.4	58.5	69.0	58
% H_2	33.6	41.5	31.0	42

action leading to the formation of ethane is quite variable and a hard one to control. The ethane content may vary from nothing up to about 65 percent of the gas mixture, the average of a large number of runs being about 25 percent. The presence of ethane was not suspected at first and the disturbing factor in the gas analytical results led to considerable investigation as to the cause, vapors of aldehyde, ether and alcohol having been in turn studied. It was found that none of these vapors were present in sufficient amounts to cause any trouble. The rate of withdrawing the gases from the reacting tube and the temperature are the main factors influencing this reaction.

In this connection it was of interest to know the behavior of mixtures of hydrogen and ethylene when passed over catalysts at the temperature of the experiments cited above. The following experiment was performed.

Ethylene and Hydrogen over TiO₂

A mixture of ethylene and hydrogen, analyzing 43 percent C_2H_4, was passed from an eight-liter bottle, provided with suitable inlet, manometer, syphon and outlet tubes, through the furnace over a layer of the catalyst. Care was taken to adjust the rate of flow uniformly, and to keep the pressures

equal in the delivery and receiving containers. In each run about 1 liter of the gas mixture was passed through. The air in the apparatus was displaced before readings were taken. Data from one run are here shown.

TABLE XIII

Duration of run	1 hr.
cc gas passed over	1000
cc gas collected	1005
% ethylene before	43.0
% ethylene after	41.0

The result shows that only slight reaction has taken place. From this we can conclude that these gases are only reactive when in the nascent state.

Ethylene over TiO_2

It was thought desirable to study the stability of ethylene, alone and also in presence of the catalytic agents, under the conditions of the experiment. The ethylene was made by the dehydration of alcohol over Al_2O_3, and was confined over saturated salt solution. The apparatus described in the preceding section was employed. The experiment was first tried without a catalyst. The temperature was 500° C. The run extended over one and a half hours and 1 liter of the gas was passed through. Data are shown below.

TABLE XIV

Temperature of furnace	500° C
cc gas passed through	1000
cc gas collected	1002
Duration of run	$1\frac{1}{2}$ hrs.
% ethylene before	98.9
% ethylene after	98 5

· At temperatures, therefore, below 500°, ethylene is not decomposed appreciably under the conditions of the experiment, without a catalytic agent. This substantiates the work of Lewes,[1] who found that decomposition did not begin

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[1] Proc. Roy. Soc., **55,** 90 (1894).

below 600°. Norton and Noyes[1] found decomposition to take place at a dull redness, the products being benzene, naphthalene, methylene, propylene and butylene, divinyl ($CH_2 = CH — CH = CH_2$) and CH_4 and C_2H_6. According to Day,[2] the change to methane and ethane takes place only after 171 hours of continuous heating to 400° C.

That ethylene is not decomposed over alumina is shown by previous experiments.

Two runs were made with TiO_2 as catalyst at a temperature of 490°. The data follow:

TABLE XV

	I	II
Duration of run	45 min.	68 min.
cc gas passed through	800	1000
cc gas collected	850	1049
% ethylene before	98.5	98.8
% ethylene after	94.6	90.9
% decomposition	4.0	7.9

TiO_2 catalyzes the decomposition to a small extent. There is a corresponding volume increase, which can be accounted for on the basis of the following equation:

$$2C_2H_4 = CH_4 + 2H_2 + 3C$$
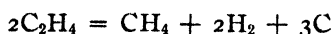
The gas residue after absorption of the ethylene on combustion in the pipette showed methane and hydrogen. The catalyst is always found covered with a black deposit of free carbon. While, therefore, this catalyst does exert some decomposing action on the pure ethylene it is not of appreciable extent.

Displacement of Equilibrium with Hydrogen

Thus far the experiments on the displacement of the equilibrium with Al_2O_3, SiO_2, ZrO_2 and TiO_2 dealt with the reversing of the ethylene-water reaction, and it was shown that the addition of water to the alcohol did cut down this

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[1] Am. Chem. Jour., **8**, 362 (1886).

[2] Ibid., **8**, 153 (1886).

reaction and that in consequence the hydrogen-aldehyde reaction was relatively increased. It was thought possible to reverse the hydrogen-aldehyde reaction by adding hydrogen to the reacting vapor.

A two-holed rubber stopper was used in place of the single-holed stopper at the inlet to the furnace tube, through one hole of which the capillary from the hydrogen container passed and through the other the tube holding the alcohol vapor. Four experiments were made with TiO_2, the conditions being kept as nearly uniform as possible. To get comparable data two runs were made with alcohol alone and two with hydrogen-alcohol mixtures. In computing the percentages of C_2H_4 and H_2 due allowance was, of course, made for the hydrogen added in order to get the actual amount formed in the decomposition.

TABLE XVI

Displacement of the hydrogen-aldehyde reaction

	Alcohol		Alcohol and hydrogen	
	I	II	III	IV
cc alcohol added	33.7	38.1	13.6	13.6
cc hydrogen added	—	—	500	500
cc gas collected	1705	1630	1240	1260
% ethylene formed	47.5	45.6	54.1	51.8
% hydrogen formed	52.5	55.4	45.9	48.2
Average % C_2H_4	46.5		53.0	
Average % H_2	53.9		47.0	

It is thus seen that whereas the hydrogen normally runs 53.9 percent with this sample of catalyst (C), the addition of free hydrogen to the alcohol vapors has the effect of reducing the amount formed to 47.0 percent. The equilibrium of the hydrogen-aldehyde reaction is thus displaced. This can be explained, as in the case of the displacement with water, by an approaching saturation of the surface of the catalyst with respect to hydrogen.

Aldehyde over TiO₂

Since acetaldehyde, CH_3CHO, is one of the products of decomposition of alcohol, being formed simultaneously with hydrogen, it is of importance to know its stability at temperatures of the experiment in presence of the catalytic agent.

Heated to about 520° C without a catalytic agent, entire decomposition took place, yielding pungent-smelling, brown croton aldehyde, $CH_3 — CH = CH — CHO$, in the condenser and a copious evolution of gas, which analyzed as follows:

<p align="center">TABLE XVII</p>

CO_2	9.6%
C_2H_4	38.0
CO	22.0
C_2H_6	3.6
CH_4	26.4

At temperatures about 400° C there is little decomposition of aldehyde. Out of 15 cc of aldehyde passed through the tube 14.5 cc were recovered unaltered in the condenser. Very little gas was given off. A sample of this, recalculated on an air-free basis, showed 57.4 percent CH_4 and 42.6 percent CO and no ethylene or ethane. Thus, while at 520° the decomposition is complete and secondary reactions set in, at 400° the decomposition is slight and takes place practically in accordance with the equation

$$CH_3CHO = CH_4 + CO.$$
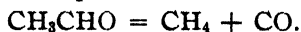
In the presence of TiO_2 at the same temperature, 400°, the decomposition is likewise very slow. The gaseous products consist of equal parts of methane and carbon monoxide. That very little action is exerted by this catalyst can further be concluded from the previous work on alcohol where it was found that the percentages of CO and CH_4 resulting from CH_3CHO did not exceed 6.7 percent in any experiment.

Ether over TiO₂ and Al₂O₃

Ether passed over Al_2O_3 at about 380° C decomposes quantitatively into ethylene and water, in accordance with the following equation:

$$\begin{array}{c} CH_3 - CH_2 \\ \diagdown \\ \diagup \\ CH_3 - CH_2 \end{array} O = 2CH_2.CH_2 + H_2O$$
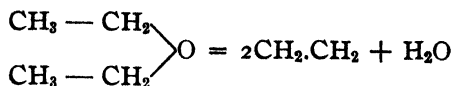
6 cc of ether yielded 2280 cc gas which analyzed 98.6 percent ethylene, the remainder being air. With TiO_2 there is a slow dehydrating action and practically all the ether is recovered in the condenser. No aldehyde or hydrogen forms.

The dehydrating action of alumina on ether is similar to that on alcohol. In fact, ether is doubtless the intermediate product formed in the dehydration of alcohol. As shown below, at 210°, ether is obtained from alcohol by dehydration with Al_2O_3. Alcohol may be considered to combine with elimination of water thus. .

$$\begin{array}{cc} CH_3.CH_2.OH & CH_3.CH_2 \\ \longrightarrow & \diagdown \\ & \diagup \\ CH_3.CH_2.OH & CH_3.CH_2 \end{array} O + H_2O.$$
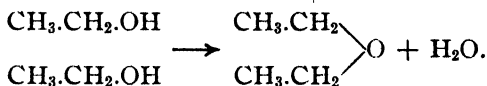
Aldehyde results only from direct dehydrogenation of alcohol.

The dehydration of alcohol by means of H_2SO_4 is the well-known method for making ether and is a classic example of catalytic action.[1] If the temperature is allowed to reach 160°-170°, the ethyl sulphuric acid formed as intermediate compound will break up into ethylene and sulphuric acid.

$$CH_3.CH_2.O.SO_3H \longrightarrow H_2SO_4 + CH_2 = CH_2.$$

Alumina, like H_2SO_4, will act on alcohol yielding ether or ethylene depending upon the temperature. At a temperature of about 210° C, 30 cc of alcohol were passed through the hot tube over Al_2O_3. Practically all the liquid was recovered in the condenser and this, subjected to fractional distillation, yielded about 75 percent ether. This is in accordance with the experiments of Senderens.[2]

Nickel as Catalyst

The catalytic action of finely divided metals, especially platinum, nickel, cobalt and copper, is well known and the decomposition of alcohols, ketones, aldehydes, etc., in presence of these metals has been investigated by Sabatier and others.

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[1] Williamson: Ann. Chim. Phys., [3] **40**, 98 (1854).

[2] Senderens: Ibid., [8] **25**, 449 (1912).

Pulverulent nickel is especially well suited for hydrogenation of many organic substances, and its action upon alcohol is one of dehydrogenation, yielding at the same time acetaldehyde in accordance with the following equation:

$$CH_3.CH_2OH \longrightarrow H_2 + CH_3CHO$$

At the temperature of the experiments aldehyde itself decomposes to a small extent into CH_4 and CO.

A study was made of the action of nickel upon alcohol, both alone and when mixed with alumina.

The finely divided nickel was prepared as follows: 100 g of nickel nitrate were heated in an evaporating dish until all moisture and nitric oxide fumes were driven off. The black oxide was then placed in a hard glass tube and heated in a combustion furnace in a stream of electrolytic hydrogen until complete reduction took place.

The catalyst thus prepared was a very powerful agent, the alcohol decomposing completely at the temperature of 380° C. The data are given in the following table.

TABLE XVIII

Temperature of furnace	380° C	Composition of gas mixture
Duration of run	15 min.	$CO_2 = 3.8\%$
Gas evolved	950 cc	$C_2H_4 = 0$
Alcohol used	1.4 cc	$CO = 3.8$
Condensate	None	$H_2 = 12.6$
		$CH_4 = 79.8$
		$C_2H_6^- = 0$

The results of the above analysis are explained as follows: The first action of the nickel is the breaking up of the alcohol into H_2 and acetaldehyde. The aldehyde is further decomposed into CH_4 and CO. At temperatures below 400° C, CO is oxidized in presence of nickel.[1]

$$2CO = CO_2 + C$$

thus accounting for the presence of CO_2 in the gas mixture. A second reaction takes place between H_2 and CO:

$$CO + 3H_2 = H_2O + CH_4$$

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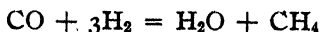
[1] Mond, Langer and Quincke: Chem. News, **62**, 95 (1890); Sabatier: "Die Katalyse in der organischen Chemie," 134 (1914).

A third reaction may also occur between some of the carbon dioxide formed above and the hydrogen:

$$CO_2 + 4H_2 = 2H_2O + CH_4$$
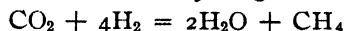
This reaction is likewise facilitated by nickel and goes on readily below 400° C. These reactions between the gases account for the high percentage of methane and corresponding lower values for H_2 and CO.

Nickel and Alumina as Catalyst

Since metallic nickel functions as a dehydrogenating catalyst and Al_2O_3 as a dehydrating agent, it was thought desirable to try mixtures of the two catalysts and thus study the combined effect of the two.

The following experiment was performed with this object in view. Equal parts by weight of $Al(NO_3)_3$ and $Ni(NO_3)_2$ were dissolved in distilled water and enough 1 : 1 NH_4OH added to precipitate both salts as the hydroxides. The gelatinous mass was then washed, filtered, dried, and ground to 200 mesh. Reduction of the nickel to the pulverulent state was accomplished in a stream of hydrogen as before. A run with alcohol was made keeping conditions as uniform as possible. The data are shown in the table.

TABLE XIX

Temperature of furnace	380° C	Composition of gas mixture
Duration of run	10 min.	CO_2 = 0
Gas evolved	350 cc	C_2H_6 = 0.6
Alcohol used up	0.5 cc	CO = 1.8
		H_2 = 13.4
		CH_4 = 84.2
		C_2H_6 = 0

The evolved gas does not differ much in composition from that obtained with nickel alone. It is known that nickel catalyzes the reaction at much lower temperatures than does alumina and the above result bears out this observation. All the alcohol is broken up by the nickel before the less active alumina has a chance to function.

As a modification of the above, another experiment was performed in which the catalyst consisted of a mechanical

mixture of powdered alumina and reduced nickel. From the results obtained, Al_2O_3 in this form seems to be more active and exerts a retarding effect upon the secondary reactions taking place. Some ethylene and ethane were formed and the CO and H_2 have partially resisted transformation. The data for this experiment are shown in Col. 3 of the summarized table.

TABLE XX

Summary for nickel

Gas	Reduced nickel	Precipitated mixture Al_2O_3 + Ni	Mechanical mixture Al_2O_3 + Ni
CO_2	3.8	0	1.4
C_2H_4	0.0	0.6	2.0
CO	3.8	1.8	29.0
H_2	12.6	13.4	29.0
CH_4	79.8	84.2	35.2
C_2H_6	0	0	3.4

The action of nickel is so much greater than alumina that it masks the latter's action almost entirely, yet the mechanical mixture is more effective as a dehydrant than the chemically precipitated mixture.

Conclusions

The following conclusions can be drawn from this work:

1. It has been shown that in the catalytic decomposition of alcohol the water-ethylene equilibrium can be displaced with Al_2O_3, SiO_2, ZrO_2, and TiO_2 as catalysts by adding water vapor to the system.

2. The hydrogen-aldehyde equilibrium can be displaced with TiO_2 as catalytic agent by adding hydrogen to the system.

3. The presence of water vapor furthermore greatly decreases the rate of decomposition, as shown by the decreased gas evolution for the aqueous mixtures; this applies to the volume of gas per cc of alcohol as well as the volume of gas per minute.

4. The rate of decomposition increases with rise in temperature. With Al_2O_3 at 380° C the rate is 78.2 cc gas per minute while at 490° C it is 426 for absolute alcohol. The corresponding percentage decomposition is 18 percent at 380° C and 94.5 percent at 490° C.

5. Alumina prepared from $Al(NO_3)_3$ retains its activity indefinitely, its action after five hours' use being only slightly reduced.

6. When equal volumes of alcohol and water vapor are passed over Al_2O_3, the amount of hydrogen formed is almost double that formed from the absolute alcohol.

7. Silica is a poor catalyst for the decomposition of alcohol. At 490° it yields 4 cc gas per minute.

8. It was found possible to reduce the ethylene content from 84.2 percent to 68.6 percent by adding water to the alcohol over SiO_2.

9. Zirconia, obtained by calcining the nitrate, is an active catalyst. With absolute alcohol it yields a gas containing 63.6 percent C_2H_4 and 3.5 percent H_2. With aqueous alcohol mixtures the composition changes to 42.5 percent C_2H_4 and 49.0 percent H_2.

10. The decomposition of alcohol over TiO_2 has been studied in detail. The activity decreases with time and increases with temperature rise.

11. The displacement of the equilibrium by the addition of water is marked with this catalyst.

12. When hydrogen is mixed with the alcohol vapors and passed over TiO_2, the amount of hydrogen formed decreases from 53.9 percent to 47.0 percent.

13. Ethane forms from ethylene and hydrogen when alcohol is decomposed over TiO_2.

14. The decomposition of aldehyde into methane and carbon monoxide does not take place to any great extent with TiO_2.

15. Ethyl ether results from the dehydration of ethyl alcohol with Al_2O_3 at 210° C.

16. Finely divided nickel decomposes alcohol into hy-

drogen and aldehyde. Acetaldehyde is easily broken up by this catalyst into CH_4 and CO and the reaction between H_2 and CO accounts for the high values for CH_4 obtained in the experiments.

The author takes this opportunity of expressing his appreciation and thanks to Professor Wilder D. Bancroft under whose cheerful guidance this work was carried out.

Cornell University

NEW BOOKS

The American Petroleum Industry. *By Raymond F. Bacon and William A. Hamor. Vols. I and II. 23 × 17 cm; pp. viii + 963. McGraw-Hill Book Company, 1916. Price: $10.00 per set net.*—"The purpose of the authors in preparing this work has been to produce a treatise which would present a comprehensive survey of the American petroleum industry, distinctly modern in every respect, and suitable not only as a general reference work for those engaged in the industry but also as a text-book for students of petroleum engineering. For these reasons the subject-matter is essentially descriptive, without, however, omitting the theoretical considerations necessary for the proper understanding of the subjects included."

The chapters are entitled. the geochemistry of petroleum; the geology of petroleum; the distribution of petroleum in the United States; the physical and chemical properties of petroleum; the history of the petroleum industry in the United States; oil-well technology; the valuation of oil properties; some commercial factors involved in the appraisement of petroleum properties; possible cause of the decline of oil wells and suggested methods of prolonging yield; efficiency in the production of petroleum; the condensation of gasoline from natural gas; refinery technology; special refinery technology; refinery engineering; hygienic considerations; some problems of the petroleum industry; the shale-oil industry; a glossary of bitumenology.

This book represents an enormous amount of work and seems to have been very well done It bids fair to become a standard reference work. Those who are more interested in miscellaneous information than in technology will be pleased with p. 796. "It has been stated that the dust from tarred roads has appeared to be more irritating to the eyes than that from untarred roads, and in 1910 an investigation of this matter was conducted in France by Truc and Fleig. It was ascertained that dust from untarred roads had only the slightest effect when sprinkled on the eyes of animals, and that dust from old tarred roads, from which the coating had more or less disappeared, gave little different effects. However, dust from old tarred roads with a well-preserved surface occasioned conjunctivitis and other lesions, while dust artificially produced from such roads gave still more severe effects. Notwithstanding the fact that bituminous vapors are said to have only a slight action upon the eye, the investigations of Truc and Fleig seemed to show that the results corresponded to the proportion of tar, as well as to the mechanical irritation produced by the dust and to the germs present. Concerning the observations, Baskerville has remarked that while bituminous dust may rapidly produce various lesions in the eyes, and may leave leucoma, the condition of the eye and the action of the sunlight are both predisposing causes. He notes that the experiments, which have been conducted on these points do not, moreover, constitute an argument against the tarring of the roads, for, when tarring is well done, it diminishes the chance of injury to the eyes."

Others will be interested in the special research problems, p. 802. "In the chemical treatment of petroleum products, systematic research with the view of ascertaining the most favorable temperature for the acid treatment of petroleum

distillates would be of great practical value as affording an indication to the refiner how to proceed under all circumstances.   A well-known problem in refining is the chemical treatment of lubricating oils in such a manner as to minimize the losses and to prevent the emulsions which result when sulphuric acid is used.   The production of persistent emulsions in the refining of petroleum is a problem to be attacked from the colloid-chemical point of view.   An economic process is wanted for isolating pure naphthenic acids of high molecular weight from waste lyes.   Another problem is the utilization of the esters from the naphthene carbo-acids contained in the residue from the alkali treatment.   A question of interest here is, what is the cause of the mal-odor of naphthenic acid, and how may these products be most effectively and economically deodorized?

"The following are some of the many other problems confronting petroleum technologists: A more rational utilization of the butanes and pentanes in natural gas gasoline and in light petroleum fractions; the separation of the vapors of light oils from steam vapors when petroleum is distilled by the introduction of superheated steam, and any steam not condensed with the oil vapors is returned to the superheater and passed again through the still; does the hot still metal exert any catalytic action in the pyrogenic decomposition of residues; the minimization of the decomposition of sulphur compounds during the distillation of petroleum containing asphalt; what rôle do sulphur compounds take in the condensation of petroleum to asphaltum; increasing the efficiency of tower stills; the rapid and effective revivification of spent fuller's earth; the separation of the aromatic and cyclic unsaturated hydrocarbons from the paraffin and naphthene hydrocarbons by a more effective or cheaper reagent than those now in use; the fractionation of petroleum residues containing paraffin wax into distillate and undecomposed amorphous wax; the elimination of gummy or asphaltic portions from wax distillate by a distillation or mechanical procedure, what constituents of a mineral oil are responsible for the lubricating power thereof, and can the lubricating properties of an oil be increased in the light of this knowledge; the prevention of the oxidation of mineral oils in transformers; products which will make emulsions with water without any oil coming to the surface; the recovery of more of the calorific value of an oil in the gas in producers, obtaining oil-gas of uniform quality during the whole of the gas-making period, and reducing the amount of the lampblack formed; and a rational plant for producing oil-gas from tar and of carbon monoxide from the residue, the mixed gases to be suitable for use in gas engines.   Then, too, notwithstanding the many processes which have been patented, methods for the solidification of petroleum and its products are still under investigation."   *Wilder D. Bancroft*

Theoretical Chemistry. *By Walter Nernst. Trans. from revised seventh German edition by H. T. Tizard. 22 × 15 cm; pp. xix + 853. New York: The Macmillan Company, 1916. Price: $5.00.*—This is a belated edition of the seventh German edition and everything in it is therefore at least five years old. The chapters on radioactivity, colloid chemistry, and photochemistry are therefore hopelessly out of date.   It is a valuable book for the student, however, even though it does not represent the knowledge of today in a good many respects. The last section in the chapter on the atomic theory, p. 438, is as important today as when it was first written.   "The electron theory allows us to form a clear

picture of the relation between the dualistic and unitary conceptions. The different elements and radicals have different chemical affinities towards the positive and negative electrons; those which have a strong tendency to combine with the positive electrons form positive groups of elements; similarly negative elements are characterized by their affinity for negative electrons. Besides this, different elements exercise a chemical attraction on each other which is not of a polar character. Accordingly, two atoms of an element may form a stable chemical compound without any action on the part of the electrons; the stability with which the two hydrogen or two nitrogen atoms unite with one another in the molecule is an example of this. The same is true of many of the compounds of the metalloids with each other, such as iodine chloride, phosphorus sulphide, and so on. So, too, the metals make numerous compounds with each other, in which we have no reason to suppose that the electrons take part. Carbon, especially, which forms a transition between the well-marked positive and negative elements, reacts with both groups of elements, and since electrons seem here to be out of the question, a purely unitary conception of the carbon compounds is possible.

"But so soon as a positive and a negative element react with one another we have separation of ions, that is, the additional separation of a massless electrically neutral molecule is associated with this chemical process; it is remarkable that this process involves a far deeper change in the ordinary behavior than one in which the electrons do not take part; while the compounds of the metals with each other retain their metallic character, and similarly, compounds of metalloids recall the properties of their components, when a metal reacts with a metalloid something entirely new and peculiar is produced. Substances like sodium chloride show the greatest possible difference of character from that of their components, and in the formation of such compounds clearly the chemical forces acting are the most intense.

"It is of course possible that in the non-polar reactions electrical forces are in the background, just as it has often been hoped to refer the Newtonian attraction to electrical phenomena, as has been accomplished with optics. That, however, is a matter of the future; at present it is necessary to distinguish the forces of polar character from unitary actions."

The translation has been fairly well done, but there has been great carelessness in regard to proper names, many of which are misspelled.

Wilder D. Bancroft

A Text-Book of Thermochemistry and Thermodynamics. *By Otto Sackur. Translated and revised by G. E. Gibson. 22 × 15 cm; pp. xvi + 439. New York: The Macmillan Company, 1917. Price: $3.50.*—The German edition was reviewed nearly five years ago (**17**, 178). The translator has made a number of changes, some of which are given in his preface. The headings of the chapters are: Introduction; the behavior of bodies on heating; the first law of thermodynamics; applications of the first law of thermodynamics; the second law of thermodynamics; thermodynamic equilibrium in general; general deductions from the two laws of thermodynamics; theory of solution; the laws of chemical equilibrium; thermodynamics and electrochemistry; thermoelectric phenomena; thermodynamics and capillarity; heat radiation; the Nernst heat theorem.

The attitude in regard to the theorem of LeChatelier is rather interesting, p. 208. "The principle of LeChatelier may now be stated as follows: If a system is in stable equilibrium the increase in the intensity factor X_r, corresponding to a given increase dx_r, in the quantity factor x_r, is smaller for a change to another state of stable equilibrium than for a change produced by altering x_r by dx_r, while all the other quantity factors remain constant. For example, if heat supplied to a system consisting of several phases and components (increase in entropy) causes the temperature to rise by T, the phases otherwise remaining unaltered, then the same amount of heat (increase in entropy) will raise the temperature by the smaller amount of dT if we keep the system in equilibrium throughout. The displacement of the equilibrium, therefore, acts as a brake on the imposed change in the intensity factor, in this case the temperature. The principle of LeChatelier thus determines the direction in which a monovariant equilibrium is displaced under the influence of a change imposed on one of the variables by which its state is determined. . . . . . All cases to which the principle of LeChatelier is applicable can be treated also by thermodynamical methods. The principle of LeChatelier is, however, usually much easier to apply, and is therefore of use whenever a knowledge of the direction of the displacement is all that is required."

One of the sections which has been completely rewritten is the one on the distribution of the energy in the spectrum, p. 392, or the determination of the emissivity of a black body for any wave-length as a function of the wave-length and the temperature. Rayleigh's radiation law is a consequence of the ordinary laws of electrodynamics and statistical mechanics and is approximately in accord with experiment for long waves and high temperatures, the agreement being better the longer the wave-length. The shorter the wave-length, however, the greater is the discrepancy between Rayleigh's law and the experimental facts. For infinitely short waves Rayleigh's formula cannot possibly be right because it calls for an infinite emissivity, when the wave-length becomes zero, whereas the emissivity of an actual black body falls off rapidly toward zero in the ultra-violet end of the spectrum. The reason for this discrepancy is not yet known with certainty. The failure of Rayleigh's law may be ascribed either to an error in the statistical calculation or to the inapplicability of the ordinary laws of mechanics to very rapid vibrations. Planck has adopted the latter view and assumes that the energy of an oscillator does not very continuously, but by finite increments or quanta of energy, each having the same value. On this basis Planck has deduced a formula which is almost identical with Rayleigh's law for long wave-lengths and with Wien's law for short wave-lengths. Planck's law represents the experimental facts better than any other law which has yet been proposed, and is probably accurate to within the experimental errors. The quantum hypothesis has also proved very fruitful in other branches of physics.

Wilder D. Bancroft

THE FORMATION OF CRYSTALS IN GELS

BY HARRY N. HOLMES

The influence of certain gels—or jellies—on crystal growth is illustrated by many crystalline minerals. It is very probable that gelatinous silicic acid was the ancestor of quartz and by gradual dehydration became hard silica rock. In the gelatinous medium reactions took place under conditions favoring the formation of crystalline veins. For example, the reduction of gold salts produced crystals of gold, veining the gel which later became quartz. A convincing part of this development can be reproduced in the laboratory. To the geologist a working method of duplicating many such processes of nature must be of great value. To the chemist a study of reactions in gels gives a useful control of relative concentrations and velocity of reactions. The pathologist finds in the subject some relation to the formation of crystalline material in animal tissue. Silicic acid gels are discussed in this paper more than any other but other gels function in a similar, though usually less effective manner.

Historical

E. Hatschek[1] did much important work in this field, attracted doubtless by the experiments of R. E. Liesegang.[2] The latter observed that if a drop of silver nitrate solution was placed on a film of gelatine gel containing potassium dichromate the precipitated silver dichromate was formed in concentric rings separated by clear intervals. This "rhythmic banding" of "Liesegang's rings" will be discussed in a later paper. Whether a disk of gel or a tube partly filled with a gel be used, the essential feature is that one substance shall diffuse into a gel containing another substance with which it reacts to form a rather insoluble compound. Rhythmic

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[1] Zeit. Kolloidchemie, **8**, 193 (1911); **10**, 77, 124, 265 (1912); **14**, 115 (1914).

[2] Zeit. anorg. Chem., **48**, 364 (1906); Zeit. phys. Chem., **59**, 444 (1907).

bands may form or, under different conditions, separate crystals of remarkable size and shape.

Hatschek and Simon[1] reduced gold salts in silicic acid gels by the use of oxalic acid, ammonium formate, ferrous sulphate, sodium sulphite, carbon monoxide, sulphur dioxide, hydrogen, ethylene, etc. When illuminating .gas was used as a reducing agent a black deposit of carbon always appeared mixed with the gold. Since graphite sometimes occurs with gold in quartz veins this experiment is suggestive.

Hatschek's usual method[2] of work was to make a 5–20% gelatine gel or a 1–5% agar gel containing, for example, a small amount of potassium dichromate. This was allowed to solidify in a test-tube and covered with a solution of silver nitrate. The silver ion slowly diffusing down into the gel reacted with the dichromate ion to form silver dichromate in small crystals. In 1911 Hatschek reported these crystals 0.5 mm long in 10 percent gelatine, lead dichromate 0.03 mm long in 2 percent agar; lead chloride 2 mm long in agar; barium carbonate 0.1 mm long in 5 percent gelatine; potassium sulphate 0.2 mm long in 5 percent gelatine. He also prepared a number of other crystalline compounds such as lead iodide, lead sulphate, lead chromate, calcium sulphate and barium silicofluoride. Later he used silicic acid gels as the media for diffusion and obtained larger crystals. In 1913 he reported lead chloride crystals 15 mm long. He was unable to make crystalline sulphides in gels.

His reduction of gold chloride in silicic acid with oxalic acid yielded beautiful crystalline gold and, by varying the conditions, colored colloidal gold.

Hatschek held that the concentration and nature of the gel determined the form and size of the crystals. The inelastic gels like silicic acid, he thought, were superior to the elastic organic gels like agar and gelatine. He wrote of "the practically universal tendency to form spherical bodies in

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[1] Jour. Soc. Chem. Ind., **31**, 439 (1912); Mining Eng. World, **37**, 280 (1912).
[2] Zeit. Kolloidchemie, **10**, 77 (1912).

agar and gelatine" although he did obtain some crystals in these media.

Hatschek made gels of silicic acid by mixing sodium silicate solutions with hydrochloric acid. The diffusion of a lead salt into this gel formed crystals of lead chloride. In similar fashion he treated sodium silicate with sulphuric acid and caused lead or calcium salts to diffuse into the gel thus forming crystalline sulphates of lead or calcium. With phosphoric acid gels he obtained crystalline phosphates of copper, calcium, and strontium.

Simon[1] grew the well known "lead tree" in a silicic acid gel containing lead acetate. A bit of zinc or tin was pressed into the top of the gel. I found that if the gel is about 0.02 N with respect to lead acetate a splendidly branching tree grows and may be handled roughly since it is supported on all sides by a solid.

Pringsheim[2] states that when two salt solutions diffuse into a gel in opposite directions the reaction does not proceed beyond a thin film if the solutions are isotonic. A hypertonic solution continues to diffuse into a hypotonic and any precipitate formed is deposited in the latter. In accord with this idea Hatschek often added indifferent substances to the solution on top of the gel in order to ensure reaction below the gel surface.

Liesegang[3] found that the older opinion that growth of a precipitate in a gel was limited to one side of the initial precipitation film did not hold for quinol on silver nitrate. I confirmed Liesegang's finding by several new examples. He also obtained silver crystals in gelatine by reducing silver nitrate with ferrous sulphate.

Gerhart[4] placed a solid reacting substance in a test-tube, covered it with a mixture of water glass and a suitable acid before the gel set, and after it bêcame solid poured a solution

[1] Zeit. Kolloidchemie, **12**, 171 (1913).
[2] Zeit. phys. Chem., **17**, 473 (1895).
[3] Zeit. Kolloidchemie, **17**, 141 (1915).
[4] Tsch. Min. Mitt., **28**, 347 (1908); **29**, 185 (1910).

of the second reacting substance on top. Both salts then diffused into the gel and met. Gerhart found alum and potassium nitrate to have considerable influence on the form of crystals deposited.

Hausmann[1] obtained crystalline halides of thallium in gelatine.

Dreaper[2] dispensed with a gel as a medium for reactions and used a single capillary tube. For example, a capillary tube filled with 3 percent lead acetate was immersed in 5 percent hydrochloric acid. Crystals of lead chloride nearly 1 mm long formed in the capillary. Sand in wide tubes functioned the same as a single capillary. Dreaper considered relative rates of diffusion and concentration of the incoming solution to be the determining factors.

Ernest Marriage[3] studied the arrangement and size of lead iodide crystals in fruit gels and jams. The various fruit jellies and jams influenced the precipitation of lead iodide in different ways and use was made of this fact in detecting adulteration of commercial products.

De Schulten,[4] by the slow admixtures of extremely dilute solutions of barium chloride and sulphuric acid, obtained crystals of barium sulphate that in a month measured 5 mm.

Deiss[5] prepared a gel of $MnHAsO_4$ by mixing equal volumes of 10 percent solutions of $MnCl_2$ and KH_2AsO_4. On standing three months rose-colored crystals of the same composition as the gel separated.

Kohler,[6] in a study of "rhythmic crystallization of sulphur," states that "the viscosity of the liquid must be so great that the rate of flow towards the crystallizing part is slower than the rate of crystallization." This compares with slowness of diffusion in a gel. .

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[1] Zeit. anorg. Chem., **40**, 110 (1904).
[2] Jour. Soc. Chem. Ind., **32**, 678 (1913); Zeit. Kolloidchemie, **12**, 14, 163 (1914).
[3] Zeit. Kolloidchemie, **11**, 1 (1912); Sci. Am. Sup., **77**, 375 (1914).
[4] Comptes rendus, **136**, 1444 (1903).
[5] Zeit. Kolloidchemie, **14**, 139 (1914).
[6] Ibid., **17**, 10 (1915).

Shulansky and Gies[1] observed that "in the putrefaction of meat crystals of ammonio-magnesium phosphate appear early and accumulate rapidly" due to bacterial activity. This paper and a similar one by Perlzweig and Gies[2] may have some bearing on the subject because of the hydrated colloid nature of animal tissue.

Braun[3] believed that certain phenomena attending the formation of sulphides and the deposition of copper in capillary spaces previously noted by A. C. Becquerel are of an electrochemical nature as Becquerel[4] had suggested. "Sur des nouveaux effects chimique produits dans les action capillaire." These phenomena are partly dependent according to W. Ostwald[5] on the semipermeability of precipitated membranes.

In a paper on "Electrostenolysis," H. N. Holmes[6] reported on electrocapillary action in insoluble powders.

The observation of Henri Becquerel that solutions of copper sulphate and sodium sulphide meeting by diffusion through a fine crack in a glass tube formed minute crystals of copper sulphide relates to Dreaper's experiment with the single capillary.

Cornu's[7] great series of papers on the significance of gels in geology are an important part of the literature.

Methods of Work

I found it convenient to mix equal volumes of solutions of sodium silicate and some acid, pouring the water glass into the acid and mixing quickly and thoroughly. Before the silicic acid set to a solid, one of the reacting salts was mixed with this solution which was then poured into test-tubes.

[1] Biochem. Bull., **3**, 45 (1913).

[2] Ibid., **3**, 69 (1913).

[3] Wied. Ann., **44** 507 (1891).

[4] Comptes rendus, **64**, 919 (1867); **65**, 51, 720 (1867); **66**, 77, 245, 766, 1066 (1868); **67**, 1081 (1868).

[5] Zeit. phys. Chem., **6**, 75 (1890).

[6] Jour. Am. Chem. Soc., **36**, 784 (1914).

[7] Zeit. Kolloidchemie, Vols. 1–5.

After the gel set the other salt solution designed to react with the first was poured on top. The solution on top should have a greater osmotic pressure than the gel to ensure reaction within the gel instead of above the surface.

The water glass used was a commercial grade known as "water white" with a density of 1.375. The ratio of the Na_2O to the SiO_2 was 1 : 3.5. When diluted to a density of 1.06 and titrated against hydrochloric acid using phenolphthalein as an indicator it was equivalent to 0.51 N acid. With methyl red as indicator the normality was 0.57.

This particular water glass was used at the 1.06 density for many experiments because weaker solutions were too slow in the set of the silicic acid. With this concentration an equal volume of N acetic acid was suitable for most of the experiments. Such a gel set over night and contained a small excess of acid. It was reasonably clear. This rather arbitrary selection really marked the lowest concentration limit for working convenience. Acetic acid 0.75 N serves as well and gives less excess acid. Several other acids were used for special purposes by the time of set varied with the acid. A partial list follows:

1.06 density sodium silicate with equal volume N acetic acid set in
6 hours
1.06 density sodium silicate with equal volume N formic acid set in
36 hours
1.06 density sodium silicate with equal volume N hydrochloric acid
set in 10 days
1.06 density sodium silicate with equal volume N sulphuric acid set
indefinite
1.06 density sodium silicate with equal volume N nitric acid set in
4 weeks

This applies only to the particular water glass described above. Considering convenience in time of set, clearness of the gel and failure to split as the gel contracts, the following table will be found more useful except in respect to acetic:

1.16 density sodium silicate with equal volume 3 N acetic acid set
in 1 hour
1.08 density sodium silicate with equal volume 3 N formic acid set
in 48 hours

1.06 density sodium silicate with equal volume 2 N hydrochloric
acid set in 5 days
1.06 density sodium silicate with equal volume 6 N sulphuric acid
set in 1 day
1.10 density sodium silicate with equal volume 2 N nitric acid set in
2 days

Temperature changes affect the time of set considerably.
I made a few tests with water glasses of different composition
and found it possible to get good results with them also. In
one the ratio of Na_2O to SiO_2 was 1 : 2, its density 1.69
and diluted to 1.06 the solution was equivalent to 0.67 N
acid with phenolphthalein as indicator. In another the
ratio of Na_2O to SiO_2 was 1 : 4, the density 1.34 and diluted
to 1.06 the solution was equivalent to 0.46 N acid.

New tables of time of set should be constructed on the
basis of the alkalinity of the particular water glass at hand.
For example, a 1.06 water glass equivalent to 0.67 N acid
must be mixed with an equal volume of more than N acetic
to give results similar to those in the table.

Pouring the mixture before it solidifies into the bend
of a U-tube gives the experimenter excellent control of condi-
tions. The two reacting solutions poured separately into the
arms of the U-tube slowly diffuse through the gel and meet,
often forming a sharp precipitation band. Any amount of
either solution can be used in this method.

Hatschek in some of his work directs that the mixture
of water glass and acid be dialyzed to free it from excess acid
and salts. Addition of very little ammonia sets the gel. In
other experiments he did not dialyze. I do not find it neces-
sary or desirable to dialyze out the acid and salts. Their in-
fluence on crystal formation or development of banding is
beneficial in most instances. In a number of experiments
I used a large excess of acid and in others added salts or non-
electrolytes to secure certain effects.

Doryland[1] suggested that a mixture of water glass and
just enough acid to make a neutral solution would set to a

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[1] Private communication.

water glass was used instead of 1.06 with the 3 N sulphuric acid. With the same reducing solution—8 percent oxalic acid—a series of splendidly colored bands of colloidal gold was obtained. The upper layer of the first bands was red, below that blue and below that green. A comparatively clear gap below this was followed by another red-blue-green zone. Usually after the first few rainbows the red was omitted. A dozen or more such bands in an ordinary test-tube was not uncommon—the upper bands measuring about 1 cm in depth. Golden crystals were dispersed all through these gels but it should be noted that the 1.06 water glass-3 N sulphuric rarely developed colored colloidal gold—only the yellow crystals.

Many variations in concentrations were tried. Excellent results were obtained with 0.5 cc of 1 percent gold chloride in 25 cc of gel but 2 cc was not so good and with much less than 0.5 cc the gold was too thin. Even 2 percent oxalic acid was effective as a reducer but a saturated solution—about 8 percent—was most satisfactory. A very little gum tragacanth mixed with the gel to reduce the gold chloride resulted in blue colloidal gold uniformly distributed.

Copper.—Perfect tetrahedrons of metallic copper were obtained in a 1.06 water glass-N acetic acid made 0.05 N with respect to copper sulphate. The gel was covered with a 1 percent solution of hydroxylamine hydrochloride. In a week or two the tetrahedrons were large enough to observe with the unaided eye. Those formed near the surface were much smaller than those at greater depths. Of course the farther the reducing solution diffused into the gel the more dilute it became. In a beam of sunlight the faces of the tetrahedrons gleamed with a splendid copper luster. In nearly all experiments one or more groups of overlapping tetrahedrons were noted. These formed in three radiating lines, making angles of 120° or in some instances of 60°, 120° and 180°. This arrangement of copper crystals is found in mineral deposits. All the other reducing solutions tried were inferior to hydroxylamine.

The presence of small amounts of glucose, cane sugar, alcohol or glycerol in the gel caused the formation of a good deal of red feathery stuff. The presence of sodium sulphate aided crystallization.

With a basic gel very different results were obtained. Glucose, a few grams to 25 cc, was mixed with a 1.08 water glass-0.5 N acetic acid gel and covered with 0.5 N copper sulphate. After a few months close bands of rather amorphous cuprous oxide extended down the gel for a distance of about 12 cm. At first the bands were yellow, but as they aged they turned to a dull red. At one time both colors were in evidence, the newer bands yellow. Near the surface of the gel a blue deposit of cupric hydroxide formed. This reaction is suggestive of Fehling's test for glucose. Of course no copper complex is used here but evidently slow diffusion permits the reduction from cupric hydroxide to cuprous oxide.

It has been suggested that this method gives opportunity for studying a reaction in its various stages. The control of concentrations and the rates of diffusion pave the way.

Using a U-tube containing a 1.10 water glass-0.5 N acetic acid gel in the bend and 0.5 N copper sulphate in one arm and 1 percent hydroxylamine in the other, blue-white bands with a yellow front appeared, later red cuprous oxide, and finally red tetrahedrons of metallic copper.

Silver Dichromate.—A 1.06 water glass-N acetic acid gel was set in the bend of a U-tube and the arms filled with 0.1 molar silver nitrate and 0.1 molar potassium dichromate. Minute dark red crystals soon formed. In one test-tube experiment a single crystal of silver dichromate measured 5 × 5 × 1 mm. This was after a few months growth. In a U-tube experiment a thin red sheet 1 cm long was found so thin that it was a clear red by transmitted light. Thicker crystals were almost black. The presence of very little gum tragacanth or starch in one of these gels hindered the formation of good crystals and favored the development of spherulites.

Lead Iodide.—Lead iodide crystals had been made by other investigators but merited further study. This is one

of the easiest to make and most spectacular of all the crystal exhibits. A 1.06 water glass-N acetic mixture containing 2 cc. of N lead acetate to every 25 cc was poured into test-tubes. After the silicic acid gel set firmly it was covered with 2 N potassium iodide. A compact layer of lead iodide quickly formed on the surface followed very soon by crystallization below the surface of the gel. In a few days fern-like fronds grew down into the gel mixed with many hexagonal plates. These concentrations may be varied with interesting results and the lead salt may be used above the gel with the potassium iodide in the gel. The first order is much better. Magnificent gold fern-fronds 8 cm in length and nearly perfect hexagons 5 mm in diameter were obtained in some experiments. In one or two tubes six hexagons grouped around a center much like the arrangement in some snow crystals. On standing in direct sunlight for several months the lead iodide crystals blacken somewhat.

Using an excess of the lead acetate as compared with the potassium iodide—for example in U-tubes pouring 0.25 N lead acetate in one arm and 0.1 N potassium iodide in the other with a gel separating the solutions, yellow-white needles and blocks of basic lead iodide formed. Some of the needles were 2 cm in length. Watts[1] states that if lead acetate in excess is mixed with potassium iodide the basic iodide forms unless sufficient acid is present to prevent. With lead nitrate the ordinary lead iodide results. When formed very slowly the yellow-white needles and blocks gleam brilliantly and seem to have a high index of refraction. Star-shaped groups and crossed stick arrangements were common. This is not the white double salt $PbI_2.KI.2H_2O$, made by Remsen and Herty[2] by the action of excess potassium iodide on lead iodide.

In U-tube experiments such concentrations as 0.25 N lead acetate and 0.1 N potassium iodide formed both the ordinary yellow hexagons and, in the arm nearer the lead

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[1] "Dictionary of Chemistry," **3**, 127.
[2] Am. Chem. Jour., **14**, 107 (1892).

acetate, the white-yellow basic crystals. In fact these concentrations could be so varied as to give first only the yellow crystals of lead iodide with a later formation of the white-yellow basic iodide. As the lead acetate diffused through the gel and met the potassium iodide these yellow hexagons formed and later as excess lead acetate diffused into this zone the white needles or blocks developed. Often a basic crystal formed touching the edge of a yellow hexagon and apparently "ate it up" as the excess lead acetate reached that point. With such proportions in the U-tube as 0.25 lead acetate and N potassium iodide only the yellow hexagons of the normal iodide form.

In a slightly basic gel such as 1.06 water glass-0.5 N acetic acid the formation of the white needles of the basic iodide was greatly favored. Dropping acid on these basic crystals instantly turned them yellow, forming the normal iodide. Using 0.25 N solutions of both lead acetate and potassium iodide in a U-tube a 1.06 water glass-0.5 N acetic acid gel developed white needles in two days, growing to a length of 2 cm in one week; a 1.06 water glass-N acetic acid gel developed yellow hexagons in two days and in one week white stars also appeared; a 1.06 water glass-2 N acetic acid gel developed yellow hexagons in two days and in several weeks no white crystals of the basic salt appeared. The last gel was too acid for a basic salt while the first gel had a slight alkaline reaction.

A little starch paste mixed with a 1.06 water glass-N acetic acid gel produced a most interesting result. The gel turned blue around the individual crystals, proving the release of free iodine. It cannot be urged that the excess acid formed hydrogen iodide which was oxidized by dissolved oxygen for in that event the gel would have turned a solid blue. It is possible that the starch intimately mixed with the lead iodide as it formed reduced part of it to lead sub-iodide. There is no question about the existence of a sub-iodide of lead as recently proved by Denham.[1]

[1] Jour. Chem. Soc., 111, 29 (1917).

A very little gum tragacanth in the silicic acid gel caused the appearance of spherulites of lead iodide and greatly hindered crystallization. In scores of experiments lead iodide showed no tendency to band in silicic acid gels although in agar well-marked bands of crystalline aggregate were the rule. Hatschek reports bands of lead iodide in silicic acid gels when he used tap water in preparing solutions attributing the effect to the bicarbonates present in the water.

Lead bromide in white twin crystals was prepared by experiments similar to those with lead iodide.

Mercuric Iodide.—A 1.06 water glass-N acetic acid gel with a 0.1 N content of potassium iodide was covered with a saturated solution of mercuric chloride—approximately 0.5 N. At once a layer of red mercuric iodide formed on the surface of the gel and later scarlet needles in a more or less banded arrangement depending on relative concentrations. Some of these needles grew to one cm in length. Separate cubes of mercuric iodide were observed in some tubes. With a suitable concentration of potassium iodide in the gel the growing mass of red crystals developed a yellow front bounded by a sharply marked surface. This zone of yellow needle crystals advanced down the tube. In reality a new yellow zone formed and the old turned red.

In time the excess of mercuric ions reached the double salt zone and reacted with the yellow salt to form the red. Since the yellow salt is rather soluble enough of it must form at the front of the advancing red column to supersaturate the solution at that point. In accord with Fick's law of diffusion the potassium iodide in the gel below the mass of crystals diffused upwards into the reacting front and when this lower reservoir became too greatly depleted the yellow front no longer formed, merely the usual red.

An excess of mercuric chloride also reacts—though not so readily—with the red mercuric iodide to form a somewhat soluble double salt. As a result the first zone of red crystals formed in the upper part of the gel finally disappeared as the excess of mercuric chloride from the solution above reached

this zone. Reversing the order, mixing the mercuric chloride in the gel and allowing the potassium iodide to diffuse down into the gel, produced a mass of red crystals as before but the red zone advanced down the tube at a rapid rate. In reality a new front formed and the excess potassium iodide readily dissolved the rear of the mercuric iodide column.

With suitable concentrations wonderful banding of red mercuric iodide was obtained. Some tubes contained forty bands in a distance of 8 cm. The spaces between the denser bands contained scattered crystals. The U-tube method was very useful here. Red bands advanced around the bend as the excess of mercuric chloride diffused into the gel. When sufficient mercuric chloride was supplied the red bands finally disappeared, leaving alternate opaque white and clear spaces in a replica of the original banding. Mercuric nitrate diffusing into similar gels produced much better banding than did mercuric chloride, possibly due to the difference in ionization. The presence of sodium nitrate aided banding considerably, as did sugar.

Sodium chloride showed a striking influence on the arrangement and form of the crystals of mercuric iodide. In proportion to the amount of sodium chloride added to the silicic acid gel the crystals of mercuric iodide became much larger and more like cubes than needles. They were farther apart and less of the banding arrangement was noticeable. In another series of experiments the acetic acid was dispensed with in making the gel. Water glass of 1.06 density and 2 N hydrochloric acid made 0.1 N with respect to potassium iodide was poured into tubes and after the silicic acid became solid was covered with saturated mercuric chloride. The red crystals of mercuric iodide formed were very large, relatively, far apart and no bands could be seen. This change was due to the influence of chlorides' for sodium chloride was formed in the reaction making the gel and in addition an unusual excess of hydrochloric acid was present. With less of the same acid the change was not so marked.

A little starch paste in the silicic acid gel caused the ap-

pearance of blue around the individual crystals proving—as with lead iodide—the presence of free iodine at the surface of the crystals. This, too, may be a reduction of the mercuric iodide by the starch.

Basic Mercuric Chloride.—In attempting to make mercuric iodide in a slightly basic gel, 1.08 water glass-0.5 N acetic acid, magnificent brown-black leaves were observed, some of them 2 cm in length. These leaves appeared in the arm of the U-tube containing the mercuric chloride. They formed very soon, before any potassium iodide could diffuse into that part of the gel. Other mercuric salts gave no such result, so to test the matter I poured a basic gel, 1.08 water glass-0.5 N acetic acid, into a test-tube and with no other added salt covered the gel with saturated mercuric chloride solution. The same shining red-brown leaves appeared. Since they could not be obtained in a gel of acid reaction or with any salt other than mercuric chloride, they were evidently one of the basic mercuric chlorides. A search of the literature justified this theory. Different basic chlorides are on record but the description of $HgCl_2.2HgO$ agrees perfectly with the crystals obtained above.

Gels of different basicity were covered with mercuric chloride solution and the crystals compared. With 1.06 water glass-0.5 N acetic (very slightly basic), the crystals were more widely scattered and at a distance of a few cm from the surface of the gel were excellent. This particular gel caused the most remarkable banding of the basic chloride. With a very basic gel the crystals were smaller and formed in a rather compact mass. A few grams of glucose in 25 cc of a slightly basic gel changed the results decidedly. Instead of the brown-red leaves a gray mass of close packed bands sharply marked appeared. In a distance of eight cm over one hundred of these bands were counted.

Silver Sulphate.—An attempt was made to produce silver dichromate by allowing N silver nitrate to diffuse into a silicic acid gel containing very dilute potassium dichromate. This particular gel was the result of mixing 1.06 water glass with

3 N sulphuric acid instead of the usual acetic acid. Immediate formation of bright red crystals at the top of the gel was observed and later the usual black-red silver dichromate deeper in the gel. Curiously enough, the bright red crystals were of an entirely different system, orthorhombic, from the triclinic silver dichromate below. They grew rapidly—in less than one hour their shape was apparent and over night they grew to a length of one cm. In a week or two, by using more concentrated silver nitrate, slabs 3 cm long were obtained, but in spite of their thickness they were a clear cherry-red. Using o.1 N silver nitrate no such orthorhombic crystals formed, only the ordinary silver dichromate. The gel had to be made with sulphuric acid and water glass. This suggested a double salt formed with the excess of silver nitrate but the difficulty was readily cleared by analysis and further experiment. Analysis showed the red orthorhombic crystals to be almost entirely silver sulphate with a very little silver chromate mixed in.

Chamot[1] states that both silver sulphate and silver chromate are orthorhombic, hence these must be mixed crystals. Gooch[2] and Autenrieth[3] observe that silver chromate is formed when excess silver nitrate reacts with a soluble dichromate, hot or cold. To test the mixed crystal explanation I omitted the potassium dichromate in another experiment and secured colorless slabs exactly like the cherry-red ones in shape and time of formation. Furthermore, by the presence of a single drop of a potassium dichromate solution in a tube of the gel a faint yellow color was made to appear in the slabs. Their depth of color was easily made to vary with the concentration of the potassium dichromate. No doubt this experiment could be extended to many other pairs of isomorphous substances. The conclusion is that when approximately N solution of silver nitrate diffuses into a silicic acid gel made from 1.06 water glass and 3 N sulphuric acid containing any small

[1] "Elementary Chemical Microscopy," 335.
[2] "Methods in Chemical Analysis," 406.
[3] Ber. deutsch. chem. Ges., 35, 2057 (1902).

amount of a soluble dichromate mixed crystals—not a double salt—of silver sulphate and silver chromate result. As the silver nitrate becomes more dilute at greater depths in the gel only the normal silver dichromate forms.

Silver Acetate.—The silver sulphate experiment is very similar to one with silver acetate. Increasing the concentration of silver nitrate to N in making a silver dichromate, I found that gels from acetic acid and water glass soon showed long colorless slabs or leaves. Omitting the potassium dichromate from the experiment and simply allowing N silver nitrate to diffuse into a 1.06 water glass-N acetic acid gel the same colorless leaves were produced again. Analysis showed them to be silver acetate. In ten minutes these crystals grew a few mm in length and over night to one cm.

By varying the acid mixed with the water glass in making the silicic acid gel and allowing approximately N silver nitrate to diffuse in, many silver salts can be obtained in crystalline form. This principle was applied by Hatschek to other compounds.

Silver phosphate formed in this manner (1.06 water glass-3 N phosphoric acid) grew in irregular yellow fronds, very much like minute ostrich plumes.

Acid potassium tartrate crystals grew rapidly when a 1.16 water glass-3 N tartaric acid gel was covered with any dilute potassium salt solution. Blocks 5 mm wide result and in several hours crystals of notable size could be counted on. Changing the concentrations somewhat, wide-branching fern growths were obtained.

Monosodium phosphate crystals formed when about 3 grams of disodium phosphate were mixed with 10 cc of a 1.10 water glass-2 N acetic acid gel. In a cool room perfect colorless rhombohedrons appeared in a few hours and grew to 6 mm width in two days. These crystals were so soluble that as the room warmed they dissolved. On cooling in the ice box they appeared again but not in such good crystals. Some of the attempts to duplicate this experiment failed.

Exact temperature and concentration conditions were not studied.

Urea nitrate crystals of large size formed rapidly when concentrated nitric acid mixed with an equal volume of water diffused into a 1.05 water glass-N acetic acid gel containing urea.

Lead chromate and basic lead chromate developed in a slightly basic gel such as 1.06 water glass-0.5 N acetic acid containing a little potassium chromate when lead acetate solution diffused into the gel. In a few weeks a 15 cm test-tube filled with orange tendrils curling around countless brighter yellow crystals of minute size. In addition much of the orange material concentrated in regular bands about 5 mm apart. Near the top of the gel an orange-red band 1 cm deep developed. This, of course, was basic lead chromate. Hatschek formed lead chromate in a gel of acid reaction and thus missed the opportunity of making the basic chromate.

Barium carbonate formed in a basic gel containing some sodium carbonate. A silicic acid gel was covered with a solution of a barium salt. The crystalline character of the deposit was not apparent for some time. White spherulites appeared to a depth of about 5 cm and then flower-shaped crystalline aggregates formed. They were very small but the crystalline character was apparent to the unaided eye.

Potassium bisulphate crystals of considerable size appeared in a gel formed by the "Hopkins process"[1] of obtaining soluble potassium salts and aluminium sulphate from feldspar. Finely ground feldspar was heated at 300° with moist potassium hydroxide. This partial decomposition of the feldspar was then completed by reaction with sulphuric acid. In commercial practice hydrochloric acid is used at this point. Using sulphuric acid in a mere laboratory experiment a silicic acid gel formed and crystals of $KHSO_4$ grew in this medium.

Sugar crystals often appear in ordinary fruit jellies. I have a number that measure about 5 × 7 × 9 mm.

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[1] Holland, Frazer and Miller: U. S. Patent, 1,196,734.

Calcium tartrate crystals of great beauty, 20 × 5 × 5 mm were easily obtained in a U-tube containing a 1.06 water glass-0.5 N acetic acid gel by filling one arm with a solution of calcium chloride and the other with a solution of tartaric acid.

Copper tartrate crystals of perfect shape and clear blue color were made by covering a 1.06 water glass-3 N tartaric acid gel with 0.5 N copper sulphate.

Zinc-ammonio chloride crystals of several cm in length were found in the gelatinous packing next the zinc wall of commercial dry cells. These colorless sheets are of the formula $ZnCl_2.2NH_3$. They were also obtained by Marignac in a Leclanché cell but not of such large size. The starch paste or other gelatinous filling next the wall of a dry cell regulated the diffusion rates of the zinc chloride and ammonia formed by the chemical action of the battery on discharge thus greatly aiding crystal development. On short periods of service with rest intervals these crystals were longer than in batteries run down by continuous service. This agrees with the time feature of the theory proposed in this paper.

Development of a Theory

Early in my work I decided that the most important feature of the favorable influence of gels on reactions forming crystals was the capillarity of the gel structure. To test this I used a layer of finely powdered silica in a U-tube, soaked it with water to dislodge air and filled one arm with a solution of potassium dichromate and the other with a solution of silver nitrate. Slow diffusion of the two salts through the capillary spaces between the silica grains allowed the formation of good crystals of silver dichromate. Later I learned that Dreaper[1] had already developed that idea, using not only a layer of sand but a single capillary tube. It may be objected that the rather great surface of finely divided silica permits an appreciable solution of silica thus filling the spaces

[1] Jour. Soc. Chem. Ind., **32,** 6781 (1913).

with a weak gel of silicic acid. Coarse sand did not serve so well.

It seemed worth while to extend somewhat the list of substitutes for gels in this work, so flowers of sulphur was substituted for sand in the above experiment. Some trouble was experienced in packing the sulphur in the bend of the U-tube and many attempts failed from too close packing for free diffusion. A platinum wire was used to dislodge the persistent air bubbles. Finally an excellent band of red crystals of silver dichromate formed where the silver ion met the dichromate ion. Barium sulphate and alundum powder served much better than the sulphur as substitutes for a gel. In fact the results with alundum were startling. Silver dichromate formed in flat needles 1 cm in length. Closely packed asbestos gave fair results. Certainly it cannot be urged that any gel was present in the experiments with a membrane of sulphur or alundum or barium sulphate.

Without doubt any compact mass of insoluble discrete particles with proper-sized capillaries will function as a gel in favoring the formation of crystals. Other influences may be present in a true gel. Adsorption, pressure[1] and solubility effects may greatly influence the capillary space results. A rather amorphous insoluble compound first formed by the meeting of two reacting substances in a relatively narrow channel may so further regulate the rates of diffusion as to give time for crystal formation of more of the same insoluble compound. In this suggestion the geologist may possibly find an explanation of the marked crystalline nature of some mineral veins. The pathologist, too, may obtain some light on the accumulation of crystalline deposits in animal tissue.

To test the theory the mouth of a small specimen tube was covered with a sheet of goldbeater's skin holding it on firmly with a rubber band. The tube had first been filled with a solution of 0.1 N potassium iodide. Care was taken to leave no air bubbles on the under side of the membrane and to rinse the outside of the tube. The tube was then immersed in a

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[1] Am. Jour. Sci., **16**, 532 (1916).

small beaker of saturated lead acetate solution. At once an almost amorphous precipitate of lead iodide appeared on the under side of the membrane and in less than a minute crystals of lead iodide fell in a beautiful gleaming shower, rapidly increasing in amount. It is very easy to secure gleaming crystals of lead iodide by cooling its hot solution but in this experiment the solutions were cold. Mixing the same solutions in a test-tube without the use of a membrane a yellow powder results.

When the more concentrated solution was placed inside the specimen tube the crystals formed on the upper surface of the membrane. This is in accord with the osmotic difference rules of Pringsheim. With less difference in concentration of the reacting solutions the reaction was much slower.

Separating solutions of silver nitrate and the potassium dichromate in this way it was a simple matter to make a gram or two of brilliant crystals of silver dichromate settling to the bottom of the tube. Possibly this method may be of some use in the preparation of pure compounds since the crystals are not mixed with an annoying gel. Other thin semipermeable membranes serve. Parchment paper is good but goldbeater's skin is most suitable.

In a number of experiments it was observed that at first a rather amorphous or, at least, fine-grained precipitate formed on the surface of the original membrane thus forming a new membrane of different capillary structure, which exerted a marked influence on rates of diffusion. The result of checking the rates of diffusion of the reacting substances was to give time enough for the growth of minute particles to crystalline size.

Barium sulphate is most annoying in quantitative analysis because of its tendency to form in slow-settling colloidal suspensions. It seemed an interesting experiment to precipitate it by the diffusion cup method and observe the rate of settling. I believed that if I placed a dilute solution of a sulphate inside the specimen tube, covered it with a gold-

beater's skin touching the surface of the solution and immersed the tube in a more concentrated solution of a barium salt that the barium sulphate formed on the under side of the membrane would be of much larger size crystals than usual and would settle rapidly. It did. Some modification of this experiment may possibly be applied to the determination of sulphates.

To carry the theory further the only need of the gold-beater's skin is to prevent sudden wholesale mixing of the solutions and mechanically sustain the rather amorphous precipitate first formed which then functions as the real active membrane. This theory is not universal in its application, for in gels excellent crystals of a number of substances formed without the appearance of a preliminary compact layer of precipitate. In these instances only the gel functions in regulating diffusion. The theory does apply, however, in the absence of a gel and in all instances where a compact precipitation band is formed.

John Johnston's[1] method of preparing crystals of increased size by the slow diffusion of two reacting solutions in a large volume of water at two widely separated points supports the theory above given. De Schulten's experiment described earlier in this paper is somewhat similar to Johnston's.

The usual gels employed in earlier investigations were: agar, gelatine and silicic acid. To this list I added the insoluble powders above described and also gels of ferric phosphate and manganese arsenate. Both of these permitted the formation of good crystals of lead iodide, silver dichromate and mercuric iodide. It is noteworthy that they are inorganic gels like silicic acid. Probably the protective colloid action of organic gels hinders crystal growth.

Summary

1. Good crystals of silver dichromate were obtained by allowing the slow diffusion of solutions of silver nitrate and potassium dichromate through flowers of sulphur. Barium

[1] Jour. Am. Chem. Soc., 36, 16 (1914).

sulphate powder served as well and alundum was even better. This confirms Dreaper's opinion that diffusion through capillary spaces other than those in a gel may be efficient in aiding crystal formation.

2. An experiment was devised to prove that in many instances the amorphous or fine-grained precipitate formed when two solutions meet acts as a membrane or network of capillaries retarding further diffusion and favoring the formation of more of the precipitate in larger crystalline particles.

3. Silicic acid gels of alkaline reaction were made by mixing sodium silicate with less than enough acid for neutralization. These basic gels made possible the production of crystalline salts not possible in a gel of acid reaction.

4. Gold in a beautifully crystalline condition was best prepared by mixing equal volumes of a water glass, 1.06 density, and 3 N sulphuric acid, adding 1 cc of 1 percent gold chloride to 25 cc of the mixture and, after solidification of the gel, covering with a solution of 8 percent oxalic acid.

Startling rainbow bands of red, blue and green colloidal gold mixed with scattered crystals resulted when the water glass was of 1.16 density. Both methods work readily and give better results than any yet recorded.

5. Perfect tetrahedrons of copper were secured by using 1 percent hydroxylamine hydrochloride to reduce dilute copper sulphate in a silicic acid gel. Peculiar aggregates of tetrahedrons similar to those found in copper deposits in nature were also observed.

All the steps of the reduction of cupric hydroxide to yellow and red forms of cuprous oxide were shown simultaneously in a series of many bands using glucose as the reducing agent in a silicic acid gel of alkaline reaction. With 1 percent hydroxylamine the same reduction was carried through the cupric hydroxide and cuprous oxide to tetrahedrons of metallic copper. This suggests a method of controlling the different steps of other reactions for study.

6. Lead iodide in perfect hexagonal plates 5 mm wide and golden fern-like growths 8 cm long were formed in silicic

acid gels. A basic lead iodide in yellow-white needles 2 cm long formed by the action of excess lead acetate on potassium iodide in a slightly acid gel and even better in a slightly basic gel. Iodine was released on the surface of crystals of lead iodide as shown by the presence of a little starch mixed with the silicic acid. Some reduction of the lead iodide must have taken place, possibly caused by the starch.

7. Red mercuric iodide in 2 cm needles or, in smaller crystals, banding in as many as forty regular bands in a distance of 8 cm was obtained by the diffusion of a mercuric chloride solution into a gel silicic acid gel containing potassium iodide. With certain concentration conditions yellow crystals formed in front of the red needles and were finally changed into the red mercuric iodide. Soluble chlorides exerted a striking influence on the size, form and arrangement of the mercuric iodide crystals.

8. Magnificent red-black crystals of a basic mercuric chloride resulted when a saturated solution of mercuric chloride diffused into a silicic acid gel of slightly basic reaction. In a very slightly basic gel these crystals were grouped in a remarkable series of bands. The presence of a little glucose exerted a marked influence, changing the color and developing over one hundred compact bands in a distance of 8 cm.

9. Silver sulphate crystals appeared in less than one hour when N silver nitrate diffused into a silicic acid gel made by mixing equal volumes of 1.06 density water glass and 3 N sulphuric acid. In a few days orthorhombic slabs 3 cm long developed. If enough potassium dichromate to make the whole gel 0.1 N molar with respect to this salt was present the long slabs were a beautiful clear red. In the presence of excess silver nitrate near the surface of the gel silver chromate was formed and since silver chromate and silver sulphate are isomorphous red mixed crystals resulted. The color of the crystals was made any depth of red by varying the concentration of the potassium dichromate in the gel. Farther below the surface of the gel the silver nitrate became less concentrated and triclinic crystals of the red-black sil-

ver dichromate appeared. In time they grew to a size of 3 cm.

10. Silver acetate grew in gleaming white sheets 2 cm long when N silver nitrate diffused into a silicic acid gel made from water glass and acetic acid. These crystals appeared in a few minutes. Such protective colloids as gum tragacanth, when present in very small amounts, twisted the straight crystals of silver acetate into fantastic shapes.

11. Basic lead chromate was made in crystalline bands by diffusion of lead acetate solution into a silicic acid gel of alkaline reaction containing potassium chromate; urea nitrate in large crystals by the diffusion of nitric acid into a silicic acid gel containing urea; perfect crystals 5 mm wide of acid potassium tartrate and perfect crystals of copper tartrate in a silicic acid gel made with tartaric acid; and monosodium phosphate in large coloress rhombohedrons by mixing disodium phosphate with a silicic acid gel.

12. Dry cells discharging on short interval service develop colorless sheets several cm long of $ZnCl_2.2NH_3$ next the zinc wall of the battery. The gelatinous paste in this part of the cell regulated the diffusion of the zinc chloride and ammonia formed by the discharge of the cell.

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CONTACT CATALYSIS. III

BY WILDER D. BANCROFT

Poisons

One of the striking things about catalysis by solids is the way in which the catalytic action of the solid may be reduced enormously by the presence of relatively small amounts of certain substances which are therefore said to poison the catalytic agents. In the contact sulphuric acid process,[1] for instance, a stage was soon reached in the laboratory where the reaction worked well with purified gases and there was no noticeable deterioration of the contact material. When the experiments were repeated on a commercial scale, the contact material soon became inert. It was found that this disastrous result was due to impurities in the burner gases. Even when present in apparently negligible amounts, these impurities play havoc with the catalytic action of the platinum. Arsenic is the most dangerous impurity and next comes mercury, while antimony, lead, iron, zinc, etc., act only in so far as they settle on and actually blanket the contact material. An amount of arsenic equal to 1-2 percent of the platinum in the contact material will destroy the catalytic action completely. In view of the enormous volumes of burner gas which are handled, it is easy to see to what an infinitesimal value the arsenic content must be reduced.

In the Deacon process for making chlorine from hydrochloric acid and oxygen, cupric chloride is the catalytic agent. This catalytic agent is very sensitive to the effect of impurities, such as sulphur dioxide, sulphur trioxide, and arsenic. It is because of this sensitiveness to sulphur dioxide that the hydrochloric acid from the Hargreaves salt-cake process cannot be used in the Deacon process. Water is also bad for the reaction, presumably because it is one of the decomposition products.[2]

[1] Knietsch: Ber. deutsch. chem. Ges., 34, 4069 (1901).

[2] Bancroft: Jour. Phys. Chem., 21, 573 (1917).

The Haber ammonia process is very susceptible to poisons. Among the harmful substances are sulphur, selenium, tellurium, phosphorus, arsenic, boron, and their compounds; many carbon compounds; lead, zinc, bismuth, tin, etc.[1] Such minute quantities of the above-mentioned substances as are to be found almost always in the present commercial products and so-called pure gases are sufficient to diminish seriously the catalytic efficiency. For instance, an impurity of 0.01 percent sulphur in iron renders it nearly useless.

"In view of these facts, every care is taken to obtain pure contact material and to free the reacting gases from all poisonous bodies. The first is a comparatively easy matter, the ordinary methods of purification of course being employed. The continuous removal of contact poisons from the reacting gases is a more difficult undertaking, particularly as chemical contingencies have brought about the replacement of the electrolytic hydrogen employed, by the impure hydrogen obtained from coal. This latter method of production depends upon the separation by liquefaction of the constituents of water-gas, hydrogen and carbon monoxide. Traces of carbon monoxide have then to be eliminated together with the gaseous impurities derived from the coal decomposition as well as the contaminations arising from the use of piping, lubricating oil in the pumps, etc. A development of this process of hydrogen production has recently been patented, in which carbon monoxide and steam are caused to interact under pressure at 300°–600°, in presence of a catalyst such as iron, nickel, and the like, thereby producing carbon dioxide and hydrogen, of which the former is removed by absorption, leaving hydrogen ready compressed for the ammonia synthesis. The nitrogen employed is usually obtained by the fractionation of liquid air.

"In general the gases are filtered, washed, and then conducted over various solid absorption agents, whilst in some cases further purification is effected by passage over a portion of the same material as is employed as catalyst, at a

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[1] Jobling: "Catalysis and Its Industrial Applications," 44 (1916).

raised temperature, before introduction into the catalyzer. This material is renewed repeatedly. The yield is found to be increased if both gases are deprived of water or of substances capable of producing water."

It is very difficult to get any definite facts in regard to the Ostwald nitric acid process. According to Jobling[1] "crude gas liquor formed the source of the ammonia first employed, the liquor being brought into contact with the hot air on the counter-current principle. The resulting mixture was purified by washing and passage over milk of lime to remove carbon dioxide and sulphuretted hydrogen. In some cases no purification was effected, the products of the combustion of sulphur compounds being easily removed from the nitric acid by a single operation, while those coming from nitrogen compounds, such as aniline, pyridine, and prussic acid themselves form nitric acid."

This statement seems very improbable, there being some who say that ammonia from by-product coke ovens cannot be used at all and that the Ostwald process became successful only when pure ammonia was used such as that from the Haber ammonia process or that obtained by the action of steam on calcium cyanamide, $CaCN_2 + 3H_2O = CaCO_3 + 2NH_6$. As a matter of fact, it is apparently not a very difficult matter to purify ammonia from the by-product coke ovens sufficiently to make it suitable for the Ostwald process. I have not been able to find any statement whether air is used because it is cheaper or because the large excess of nitrogen helps to check the oxidation of ammonia to nitrogen.

In the Sabatier hydrogenation process it is indispensable to success[2] that "the materials, whether hydrogen, metal, or organic compound, must be as pure as can be obtained, for any impurity is readily adsorbed by the catalyst to the detriment of its activity. Sulphur and its volatile compounds, as well as the halogens,[3] are particularly to be avoided in this

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[1] "Catalysis and Its Industrial Applications," 47 (1916).

[2] Jobling: Ibid., 69 (1916).

[3] [The nickel oxide must not be prepared from the chloride because of the great difficulty of washing out the last traces of adsorbed chloride.]

respect, and, to a lesser degree, arsenic and phosphorus with their volatile compounds. Electrolytic hydrogen, or hydrogen of equivalent purity, appears to be essential. Even then the catalyst must, sooner or later, succumb to the toxic effects of minute impurities impossible to remove; in consequence, the desirability of frequent renewal needs emphasis."

The platinum catalysis of hydrogen peroxide solutions is poisoned by very many things[1]—hydrocyanic acid, iodine dissolved in potassium iodide, mercuric chloride, hydrogen sulphide, mercuric cyanide, carbon monoxide, hydroxylamine hydrochloride, aniline, hydrochloric acid, etc.

Since one or more of the reacting substances must be adsorbed by the solid catalytic agent for catalysis to take place, the poisoning must be due to decreased adsorption. We shall have an apparent poisoning of the catalytic agent if we have formed on it a solid, liquid, or gaseous film which cuts down the adsorption of the reacting substances. Berliner[2] has described some experiments on the adsorption of hydrogen by palladium foil which bring out clearly the enormous effect due to very slight amounts of impurity. "A piece of palladium foil, weighing 44.5 mg, which had not been ignited or purified on the surface by mechanical treatment, adsorbed no hydrogen in the course of several hours. When the metal was treated in a vacuum, 450 cubic millimeters of gas were set free, 114 times the volume of the palladium. After the apparatus had stood for two hours, hydrogen was let in but no perceptible adsorption took place. When the foil was removed from the apparatus, careful observation showed that the surface was not clean, as was shown by the fact that water did not wet the palladium. It seems probable that the trouble was due to vapors of fats in the apparatus or to fat carried to the metal by capillary action. To test this, the foil was ignited in the blast lamp; when cold it was wetted at once by water. After standing one hour in the apparatus, the surface was so coated with a film of fat that the foil was not wetted

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[1] Bredig: Zeit. phys. Chem., **31**, 324 (1899).

[2] Wied. Ann., **35**, 803 (1888).

by water any more. To prove that the surface impurities
kept the metal from absorbing hydrogen, the palladium was
cleaned by being made the positive electrode in sulphuric
acid. After being washed with water and dried between
filter paper, the metal was put into the apparatus as quickly
as possible and hydrogen let in at once. The palladium ad-
sorbed 857 times its volume of hydrogen almost instantaneously.
The metal can also be purified by igniting in the blast lamp.
The foil was taken out of the apparatus and ignited in the
blast lamp. If put back quickly into the apparatus and hy-
drogen let in at once, the metal adsorbed 860 times its volume
of hydrogen. If there was a delay of an hour or two before
the hydrogen was let into the apparatus, no adsorption took
place. Similar results were obtained with platinum."

    Berliner called attention to the importance of these re-
sults as affecting the catalytic action of metals; but his work
does not seem to have made much impression in spite of the
fact that the platinum used in making contact sulphuric acid
is readily poisoned by minute quantities of arsenic, etc. The
quantitative part of Berliner's work on the adsorption of
hydrogen and oxygen has been criticized severely by Ramsay,
Mond and Shields[1] because of the very small volumes of gas
with which Berliner worked.

    Bodenstein[2] found that traces of fat cut down the rate
at which platinum accelerates the formation of water from
oxyhydrogen gas. The most intense action occurs only when
the platinum surface is very clean, and can be obtained in a
reproducible manner only when the purity of the surface is a
maximum, a state of things which is very difficult to obtain
and almost impossible to maintain. "The purification of
the platinum was done at first by heating with concentrated
sulphuric acid or with a mixture of nitric and sulphuric acids,
later by treating with a mixture of chromic and sulphuric
acids, followed by washing with freshly distilled water, which
was protected as much as possible from contamination by the

    [1] Zeit. phys. Chem., **19,** 58 (1906).

    [2] Ibid., **46,** 730 (1903).

ordinary laboratory gases. The platinum was placed in the apparatus while still moist and was then brought in contact with the gases which were either not dried at all or were dried slightly by passing over calcium chloride. After the first difficulties had been overcome, reproducible results could almost always be obtained in this way.

"In order that the effectiveness of the platinum might be kept constant, all the other parts of the apparatus were of course kept scrupulously clean. The large joints, including one with 5 cm opening through which the platinum ball was at first introduced, were ground so carefully that when moist they closed absolutely gas-tight and therefore never needed to be greased. Vapor from the mercury in the manometer could not be kept out however, and the stopcock on the gasometer could not be made tight without the use of grease. I tried, of course, to use glassy phosphoric acid as lubricating medium; but it becomes diluted too rapidly in the moist gases and then the joint is not tight any more. Consequently the effectiveness of the platinum always decreased gradually, though so slowly in the successful experiments that the results are comparable. In the experiments with an excess of oxygen, the catalytic action of the platinum once remained constant for several days. This looks as though the chief disturbing factor were the grease from the stopcock, which was oxidized in this case."

It has been pretty well understood for eighty years or more that impurities cut down the catalytic action of platinum. Faraday[1] is very clear on this point. "During the course of the experiments made to render the instrument [voltameter] efficient, I was occasionally surprised at observing a deficiency of the gases resulting from the decompositions of water, and at last an actual disappearance of portions which had been evolved, collected and measured. The circumstances of the disappearance were these. A glass tube, about twelve inches in length and three quarters of an inch in diameter, had two platina poles fixed into its upper, hermetically sealed,

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[1] "Experimental Researches in Electricity," 1, 165 (1839).

extremity: the poles, where passed through the glass, were of wire; but terminated below in plates, which were soldered to the wires with gold. The tube was filled with dilute sulphuric acid; a voltaic battery was connected with the two wires, and sufficient oxygen and hydrogen evolved to occupy four-fifths of the tube, or, by the graduation, 116 parts. On separating the tube from the voltaic battery the volume of gas immediately began to diminish, and in about five hours only about 13.5 parts remained, and these ultimately disappeared.

"It was found by various experiments, that this effect was not due to the escape or solution of the gas, nor to re-combination of the oxygen or hydrogen in consequence of any peculiar condition *they* might be supposed to possess under the circumstances; but to be occasioned by the action of one or both of the poles within the tube upon the gas around them. On disuniting the poles from the pile after they had acted upon dilute sulphuric acid, and introducing them into separate tubes containing mixed oxygen and hydrogen, it was found that the positive pole [the anode] effected the union of the gases, but the negative pole apparently not. It was ascertained also that no action of a sensible kind took place between the positive pole with oxygen or hydrogen alone. These experiments reduced the phenomena to the consequence of a power possessed by the platina, after it had been the positive pole of a voltaic pile, of causing the combination of oxygen and hydrogen at common, or even at low temperatures. . . .

"The act of combination always seemed to diminish, or apparently exhaust, the power of the platina plate. It is true, that in most if not all instances, the combinations of the gases, at first insensible, gradually increased in rapidity, and sometimes reached to explosion; but when the latter did not happen, the rapidity of combination diminished; although fresh portions of gas were introduced into the tubes, the combination went on more and more slowly, and at last ceased altogether. The first effect is an increase in the rapidity of combination dependent in part upon the water flowing off from the platina plate, and allowing a better contact with the gas, and in part

upon the heat evolved during the progress of the combination. But, notwithstanding the effect of these causes, diminution, and at last cessation of the power, always occurred. It must not, however, be unnoticed, that the purer the gases subjected to the action of the plate, the longer was its combining power retained. With the mixture evolved at the poles of the voltaic pile, in pure dilute sulphuric acid, it continued longest; and with oxygen and hydrogen, of perfect purity, it probably would not be diminished at all. . .

"These experiments led to the expectation that the power of causing oxygen and hydrogen to combine, which could be conferred upon any piece of platina by making it the positive pole of a voltaic pile, was not essentially dependent upon the action of the pile, or upon any structure or arrangement of parts it might receive whilst in association with it, but belonged to the platina *at all times*, and was *always effective* when the surface was *perfectly clean*. And though, when made the *positive* pole of the pile in acids, the circumstances might well be considered as those which would cleanse the surface of the platina in the most effectual manner, it did not seem impossible that ordinary operations would produce the same result, although in a less eminent degree. Accordingly a platina plate was cleaned by being rubbed with a cork, a little water, and some coal-fire ashes upon a glass plate; being washed, it was put into mixed oxygen and hydrogen, and was found to act at first slowly, and then more rapidly. In an hour, a cubical inch and a half had disappeared. Other plates were cleaned with ordinary sand-paper and water; others with chalk and water; others with emery and water; others, again, with black oxide of manganese and water; and others with a piece of charcoal and water. All of these acted in tubes of oxygen and hydrogen, causing combination of the gases. The action was by no means so powerful as that produced by plates having been in communication with the battery; but from one to two cubical inches of the gases disappeared, in periods extending from twenty-five to eighty or ninety minutes.

"Upon cleaning the plates with a cork, ground emery, and

dilute sulphuric acid, they were found to act still better. In order to simplify the conditions, the cork was dismissed, and a piece of platina foil used instead; still the effect took place. Then the acid was dismissed, and a solution of *potassa* used, but the effect occurred as before. These results are abundantly sufficient to show that the mere mechanical cleansing of the surface of the platina is sufficient to enable it to exert its combining power over oxygen and hydrogen at common temperatures.

"I now tried the effect of heat in conferring this property upon platina. Plates which had no action on the mixture of oxygen and hydrogen were heated by the flame of a freshly trimmed spirit lamp, urged by a mouth blow-pipe, and when cold were put into tubes of the mixed gases: they acted slowly at first, but after two or three hours condensed nearly all the gases. A plate of platina, which was about one inch wide and two and three-quarters in length, and which had not been used in any of the preceding experiments, was curved a little so as to enter a tube, and left in a mixture of oxygen and hydrogen for thirteen hours; not the slightest action or combination of the gases occurred. It was withdrawn at the pneumatic trough from the gas through the water, heated red hot by the spirit lamp and blow-pipe, and then returned when cold into the *same* portion of gas. In the course of a few minutes, diminution of the gases could be observed, and in forty-five minutes about one cubical inch and a quarter had disappeared. In many other experiments platina plates when heated were found to acquire the power of combining oxygen and hydrogen.

"But it happened not infrequently that plates, after being heated, showed no power of combining oxygen and hydrogen gases, though left undisturbed in them for two hours. Sometimes also it would happen that a plate which, having been heated to dull redness, acted feebly, upon being heated to whiteness, ceased to act; and at other times a plate which, having been slightly heated, did not act, was rendered active by a more powerful ignition. Though thus uncertain in its action, and though often diminishing the power given to the

plates at the positive pole of the pile, still it is evident that heat can render platina active, which before was inert. The cause of its occasional failure appears to be due to the surface of the metal becoming soiled, either from something previously adhering to it, which is made to adhere more closely by the action of the heat, or from matter communicated from the flame of the lamp itself, or from the air itself. It often happens that a polished plate of platina, when heated by the spirit lamp and a blow-pipe, becomes dulled and clouded on its surface by something either formed or deposited there; and this, and much less than this, is sufficient to prevent it from exhibiting the curious power now under consideration. Platina also has been said to combine with carbon; and it is not at all unlikely that in processes of heating, where carbon or its compounds are present, a film of such a compound may be thus formed, and thus prevent the exhibition of the properties belonging to *pure* platina. When heat does confer the property it is only by the destruction or dissipation of organic or other matter which had previously soiled the plate."

It does not strike Faraday as especially remarkable that a liquid or a solid should cut down the catalytic action of platinum but it puzzles him very much when he finds the same phenomena occurring with a gas.[1]

"Clean platina, by which I mean such as has been made the positive pole of a pile, or has been treated with acid, and has then been put into distilled water for twelve or fifteen minutes, has a *peculiar friction* when one piece is rubbed against another. It wets freely with pure water, even after it has been shaken and dried by the heat of a spirit lamp; and if made the pole of a volatile pile in a dilute acid, it evolves minute bubbles from every part of its surface. But platina in its common state wants that peculiar friction; it will not wet freely with water as the clean platina does, and when made the positive pole of a pile, it for a time gives off large bubbles, which seem to cling or adhere to the metal, and are evolved at distinct and separate points of the surface. These appearances and effects,

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[1] Faraday: "Experimental Researches on Electricity," **1**, 185 (1839).

as well as its want of power on oxygen and hydrogen, are the consequences, and the indications, of a soiled surface.

"I found also that platina plates which had been cleaned perfectly soon became soiled by mere exposure to the air; for after twenty-four hours they no longer moistened freely with water, but the fluid ran up into portions, leaving part of the surface bare, whilst other plates which had been retained in water for the same time, when they were dried did moisten, and gave the other indications of a clean surface. Nor was this the case with platina or metals only, but also with earthy bodies. Rock crystal and obsidian would not wet freely upon the surface, but being moistened with strong oil of vitriol, then washed, and left in distilled water to remove all the acid, they did freely become moistened, whether they were previously dry or whether they were left wet; but being dried and left exposed to the air for twenty-four hours, their surface became so soiled that water would not then adhere freely to it, but ran up into partial portions. Wiping with a cloth (even the cleanest) was still worse than exposure to air; the surface either of the minerals or metals immediately became as if it were slightly greasy. The floating upon water of small particles of metals under ordinary circumstances is a consequence of this kind of soiled surface. The extreme difficulty of cleaning the surface of mercury when it has once been soiled or greased, is due to the same cause.

"The same reasons explain why the power of the platina plates in some circumstances soon disappear, and especially upon use. MM. Dulong and Thenard[1] have observed the same effect with the spongy metal, as indeed have all those who have used Doebereiner's instantaneous light machines. If left in the air, if put into ordinary distilled water, if made to act upon ordinary oxygen and hydrogen, they can still find in all these cases *that* minute portion of impurity which, when once in contact with the surface of the platina, is retained there, and is sufficient to prevent its full action upon oxygen and hydrogen at common temperatures. A slight elevation of tem-

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[1] Ann. Chim. Phys., **24**, 386 (1823).

perature is again sufficient to compensate this effect, and cause combination.

"No state of a solid body can be conceived more favorable for the production of the effect than that which is possessed by platina obtained from the ammonio-muriate by heat. Its surface is most extensive and pure, yet very accessible to the gases brought in contact with it. If placed in impurity, the interior, as Thenard and Dulong have observed, is preserved clean by the exterior; and as regards temperature, it is so bad a conductor of heat, because of its divided condition, that almost all which is evolved by the combination of the first portions of gas is retained within the mass, exalting the tendency of the succeeding portions to combine.

"I have now to notice some very extraordinary interferences with this phenomena, dependent not upon the nature or condition of the metal or other acting solid, but upon the presence of certain substances mingled with the gases acted upon; and as I shall have occasion to speak frequently of a mixture of oxygen and hydrogen, I wish it always to be understood that I mean a mixture composed of one volume oxygen to two volumes of hydrogen, being the proportions that form water. Unless otherwise expressed, the hydrogen was always that obtained by the action of dilute sulphuric acid on pure zinc, and the oxygen that obtained by the action of heat from the chlorate of potassa. Mixtures of oxygen and hydrogen with *air*, containing one-fourth, one-half, and even two-thirds of the latter, being introduced with prepared platina plates into tubes, were acted upon almost as well as if no air were present; the retardation was far less than might have been expected from the mere dilution and consequent obstruction to the contact of the gases with the plates. In two hours and a half nearly all the oxygen and hydrogen introduced as mixture was gone.

"But when similar experiments were made with *olefiant gas* (the platinum plates having been made the positive poles of a voltaic pile in acid), very different results occurred. A mixture was made of 29.2 volumes hydrogen and 14.6

volumes oxygen, being the proportions for water; and to this was added another mixture of 3 volumes oxygen and one volume olefiant gas, so that the olefiant gas formed but $1/_{48}$th part of the whole. Yet this mixture in the platina plate would not act in forty-five hours. The failure was not for want of any power in the plate, for when after that time it was taken out of this mixture and put into one of oxygen and hydrogen, it immediately acted, and in seven minutes caused explosion of the gas. This result was obtained several times, and when larger proportions of olefiant gas were used, the action seemed still more hopeless. A mixture of forty-nine volumes oxygen and hydrogen with one volume of olefiant gas had a well-prepared platina plate introduced. The diminution of gas was scarcely sensible at the end of two hours, during which it was watched; but on examination twenty-four hours afterwards, the tube was found blown to pieces. The action, therefore, though it had been very much retarded, had occurred at last, and risen to a maximum. With a mixture of ninety-nine volumes of oxygen and hydrogen with one volume of olefiant gas, a feeble action was evident at the end of fifty minutes; it went on accelerating until the eighty-fifth minute, and then became so intense that the gas exploded. Here also the retarding effect of the olefiant gas was very beautifully illustrated.

"Plates prepared by alkali and acid produced effects corresponding to those just described. It is perfectly clear from these experiments, that *olefiant gas*, even in small quantities, has a very remarkable influence in preventing the combination of oxygen and hydrogen under these circumstances, and yet without at all injuring or affecting the power of the platina.

"Another striking illustration of similar interference may be shown in *carbonic oxide*, especially if contrasted with *carbonic acid*. A mixture of one volume oxygen and hydrogen with four volumes of carbonic acid was affected at once by a platina plate prepared with acid, etc., and in one hour and a quarter nearly all the oxygen and hydrogen was gone. Mix-

tures containing less carbonic acid were still more readily affected. But when carbonic oxide was substituted for the carbonic acid, not the slightest effect of combination was produced; and when the carbonic oxide was only one-eighth of the whole volume, no action occurred in forty and fifty hours. Yet the plates had not lost their power, for being taken out and put into pure oxygen and hydrogen, they acted well and at once. Two volumes of carbonic oxide and one of oxygen were mingled with nine volumes of oxygen and hydrogen. This mixture was not affected by a plate which had been made positive in acid, though it remained in it fifteen hours. But when to the same volumes of carbonic oxide and oxygen were added thirty-three volumes of oxygen and hydrogen, the carbonic oxide being then only $1/18$th part of the whole, the plate acted, slowly at first, and at the end of forty-two minutes the gases exploded.

"These experiments were extended to various gases and vapours, the general results of which may be given as follows: Oxygen, hydrogen, nitrogen, and nitrous oxide, when used to dilute the mixture of oxygen and nitrogen, did not prevent the action of the plates even when they made four-fifths of the whole volume of gas acted upon. Nor was the retardation so great in any case as might have been expected from the mere dilution of the oxygen and hydrogen, and the consequent mechanical obstruction to its contact with the platina. The order in which carbonic acid and these substances seemed to stand was as follows: the first interfering least with the action—*nitrous oxide, hydrogen, carbonic acid, nitrogen, oxygen;* but it is possible the plates were not equally well prepared in all the cases, and that other circumstances also were unequal. Consequently, more numerous experiments would be required to establish the order accurately.

"As to cases of *retardation*, the powers of olefiant gas and carbonic oxide have been already described. Mixtures of oxygen and hydrogen, containing from $1/16$th to $1/20$th of sulphuretted hydrogen or phosphuretted hydrogen, seemed to show a little action at first, but were not further affected by the

prepared plates, though in contact with them for seventy
hours. When the plates were removed they had lost all
power over pure oxygen and hydrogen, and the interference of
these gases was therefore of a different nature from that of
the two former, having permanently affected the plate. A
small piece of cork was dipped in sulphuret of carbon and
passed up through water into a tube containing oxygen and
hydrogen, so as to diffuse a portion of its vapour through the
gases. A plate being introduced appeared at first to act a
little, but after sixty-one hours the diminution was very small.
Upon putting the same plate into a pure mixture of oxygen
and hydrogen, it acted at once and powerfully, having ap-
parently suffered no diminution of its force.

"A little vapour of ether being mixed with the oxygen
and hydrogen retarded the action of the plate, but did not
prevent it altogether. A little of the vapour of the condensed
oil-gas liquor[1] retarded the action still more, but not nearly
so much as an equal volume of olefiant gas would have done.
In both these cases it was the original oxygen and hydrogen
which combined together, the ether and the oil-gas vapour
remaining unaffected, and in both cases the plates retained the
power of acting on fresh oxygen and hydrogen. Spongy
platina was then used in place of the plates, and jets of hy-
drogen mingled with the different gases thrown against it
in air. The results were exactly of the same kind, although
presented occasionally in a more imposing form. Thus,
mixtures of one volume of olefiant gas or carbonic oxide with
three of hydrogen could not heat the spongy platina when the
experiments were commenced at common temperatures;
but a mixture of equal volumes of nitrogen and hydrogen acted
very well, causing ignition. With carbonic acid the results
were still more striking. A mixture of three volumes of that
gas with one of hydrogen caused *ignition* of the platina, yet
that mixture would not continue to burn from the jet when
attempts were made to light it with a taper. A mixture of
seven volumes of carbonic acid and *one* of hydrogen will thus

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[1] Phil. Trans., **115**, 440 (1825).

cause the ignition of cold spongy platina, and yet, as if to supply a contrast, than which none can be greater, *it cannot burn at a taper*, but causes the extinction of the latter. On the other hand, the mixtures of carbonic oxide or olefiant gas, which can do nothing with the platina, are *inflamed* by the taper, burning well.

"Hydrogen mingled with the vapour of ether or oil-gas liquor causes the ignition of the spongy platina. The mixture with oil-gas burns with a flame far brighter than that of the mixture of hydrogen and olefiant gas already referred to, so that it would appear that the retarding action of the hydrocarbons is not at all in proportion merely to the quantity of carbon present.

"In connection with these interferences, I must state that hydrogen itself, prepared from steam passed over ignited iron, was found when mingled with oxygen to resist the action of platina. It had stood over water seven days, and had lost all fetid smell; but a jet of it would not cause the ignition of spongy platina, commencing at common temperatures; nor would it combine with oxygen in a tube either under the influence of a prepared plate or of spongy platina. A mixture of one volume of this gas with three of pure hydrogen, and the due proportion of oxygen, was not affected by plates after fifty hours. I am inclined to refer the effect to carbonic oxide present in the gas, but have not had time to verify the suspicion. The power of the plates was not destroyed. Such are the general facts of these remarkable interferences. Whether the effect produced by such small quantities of certain gases depends upon any direct action which they may exert upon the particles of oxygen and hydrogen, by which the latter are rendered less inclined to combine, or whether it depends upon their modifying the action of the plate temporarily (for they produce no real change of it), by investing it through the agency of a stronger attraction than that of the hydrogen, or otherwise, remains to be decided by more extended experiments."

Turner[1] was on the right track when he said that "one is tempted to suppose that these gases act by soiling the metallic surface, though in some respects this is not satisfactory." This explanation was premature, however,· and a different one was offered later by Henry[2] who· amplified Faraday's experiments, correcting some of his results. Henry found that adding carbon monoxide to a mixture of hydrogen and oxygen in presence of platinum does not actually prevent the reaction between hydrogen and oxygen but retards it, so that the reaction takes place very slowly and most of the oxygen reacts with the carbon monoxide. Starting with the mixture $2CO + 2H_2 + O_2$ Henry found that about ninety percent of the oxygen reacted with the carbon monoxide and only about ten percent with the hydrogen. When the ratio of hydrogen to carbon monoxide was increased in the original mixture less of the oxygen reacted with the carbon monoxide. Faraday had found that a mixture of carbon monoxide and oxygen did not react appreciably in several days when in contact with a clean platinum plate but Henry found that a reaction does take place in presence of platinum foil, platinum sponge, and platinum black. The reaction is very slow with platinum foil, more rapid with platinum sponge and fastest of all with platinum black. Since hydrogen and oxygen react much more rapidly in presence of platinum than do carbon monoxide and oxygen, one would naturally expect preferential burning of hydrogen from a mixture of hydrogen and carbon monoxide whereas one actually gets preferential burning of carbon monoxide. Henry recognized this difficulty and met it in a very clever way though his argument is not absolutely sound.

"An obvious objection, however, presents itself to the view that carbonic oxide possesses a stronger affinity for oxygen than hydrogen exerts, viz., that while hydrogen and oxygen are speedily detonated at common temperatures by the plate or sponge, the union of carbonic oxide and hydrogen

¹ "Chemistry," 5th Ed., 647.
² Phil. Mag., [3] 9, 324 (1836).

takes place with great slowness. The explanation of this apparent anomaly, I believe to be, that the product of the combustion of hydrogen (aqueous vapor) at once quits the surface of the metal and is liquefied by the cold sides of the tube; while the combustion of the carbonic oxide yields a gas which remains for a while adherent to the metallic surface next to which it is generated, and thereby prevents a sufficiently rapid access of fresh unaltered gas to elevate materially the temperature of the platina. In confirmation of this view I found that caustic potassa, by absorbing the carbonic acid as it is formed, accelerates the acidification of carbonic oxide. When the metallic superficies is so extensive (for instance, in the powder of Liebig) that a high temperature is attained quickly by the metal in contact with the first portions of gas that are consumed, it has been shown already that carbonic oxide, like hydrogen, unites with oxygen with incandescence. Finally it is well known that even mixtures of hydrogen and oxygen do not detonate on first admitting the prepared plate. During the first minute the union is generally very slow, and it only becomes explosive when the temperature of the plate has been raised by its action upon the gaseous mixture."

It is interesting to note that Kohlschütter[1] has used a similar argument to account for what seems to be the reverse of this. Kohlschütter was studying the reduction of silver oxide by carbon monoxide or hydrogen. He points out that "with carbon monoxide the reaction begins where the gas first comes in contact with the oxide, spreads over the surface, and then takes place in the inner parts of the mass. With hydrogen the reaction begins at some point where the silver oxide is in contact with the containing vessel, usually at the bottom of the mass. While the reaction goes completely to an end with carbon monoxide, silver cannot be reduced completely by hydrogen at a moderate temperature in a single operation. This difference is probably connected with the difference in reaction products. The other product besides silver is carbon dioxide in the first case and water in

[1] Liebig's Ann., **398,** 16 (1913).

the other. Being an easily condensible vapor, water is adsorbed more strongly than carbon dioxide. It forms a film over the surface of the silver oxide and prevents the hydrogen from reacting with it."

Although the reaction between carbon monoxide and oxygen is practically irreversible at ordinary temperatures, Henry recognized that the presence of the reaction product might slow up the reaction and he proves it by removing the carbon dioxide with caustic potash, thereby increasing the reaction velocity. That was very clever of him, because most people nowadays would have been so hampered by their incomplete theoretical knowledge of reaction velocities that they would have been certain that the reaction products could not affect the reaction velocity. Henry's argument is unsound, however, in several respects. In the first place he has not shown that carbon monoxide and oxygen react more rapidly than hydrogen and oxygen when the carbon dioxide is removed continuously. He has shown that there is an increase in reaction velocity but not that the increase is sufficient to account for the phenomena. In the second place, the rate of oxidation of the carbon monoxide cannot be the determining factor because Henry obtained preferential burning of carbon monoxide in the absence of alkali. What happens is that the adsorption of carbon monoxide by platinum cuts down the adsorption of hydrogen to such an extent that the reaction between hydrogen and oxygen becomes almost negligible.

This is not an especially surprising result. Freundlich[1] points out that the general rule for mixtures of gases seems to be that the more readily adsorbed gas displaces the other to some extent and is adsorbed to a greater relative amount than one would have predicted from experiments on the single gases. This cannot be anything more than a first approximation because with readily condensible gases one of the vapors may help carry down the other. Cases of this sort have been

[1] "Kapillarchemie," 99 (1909).

studied by Hunter,[1] the most striking instance being water and ammonia. It is probable that the adsorbed water dissolves or adsorbs ammonia thus increasing the amount of ammonia apparently held by the charcoal. Bergter[2] claims that at pressures of about 5 mm the presence of oxygen increases the adsorption of nitrogen by charcoal. Displacements also occur when two solutes may be adsorbed from solution. Schmidt[3] has studied the simultaneous adsorption of iodine and acetic acid by charcoal from solutions in water and in ethyl acetate. With both solvents less of each substance was adsorbed than if the other had not been present. Schmidt generalizes to the effect that "when charcoal is in contact with a solution containing the two solutes A and B, it adsorbs less of each than when it is treated with the same substances A and B singly. If charcoal is in equilibrium with any substance A dissolved in any solvent, the addition of a second substance B will force some of A out of the charcoal and vice versa. The total amount which is adsorbed when two solutes are present simultaneously in solution is always less than the arithmetical sum of the amounts of these substances that would be adsorbed singly."

This generalization is undoubtedly too broad. A more careful study will show that the special properties of the substances A and B will have to be taken into account and that we shall find cases where the total adsorption will be greater than the sum of the single adsorptions, though no such cases seem as yet to be on record. Lake[4] has shown that one acid dye does not apparently displace another on wool or silk; but of course the absolute concentrations are very small in these cases. Freundlich and Masius[5] studied the adsorption of pairs of organic acid and obtained results similar to those of Schmidt. They also found that the acid, which is adsorbed the more, is displaced the less when the two acids are present

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[1] Jour. Chem. Soc., **23,** 73 (1870).
[2] Drude's Ann., **37,** 506 (1912).
[3] Zeit. phys. Chem., **74,** 730 (1910).
[4] Jour. Phys. Chem., **20,** 761 (1910).
[5] "Van Bemmelen Gedenkboek," 88 (1910).

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in the solution. These experiments of Schmidt and of Freund-
lich and Masius, throw light on Skey's results with nitric
and sulphuric acids. Skey[1] found that small amounts of
nitric acid were adsorbed completely from dilute solutions of
sulphuric acid but not from concentrated ones. With in-
creasing relative concentration of sulphuric acid, we should
expect an increasing displacement of nitric acid from the
charcoal which is what actually occurred.

Rona and Michaelis[2] have studied the effect of acetone
and acetic acid on the adsorption of grape sugar by charcoal.
When 100 cc of a 1.04 percent sugar solution was shaken with
5 grams charcoal, the filtrate contained only 0.53 percent
sugar. If the sugar solution contained 0.3, 3.0 or 15.0 cc
acetone, the percentages of sugar in the filtrate were 0.64,
0.97, and 1.06, respectively. If 0.2, 1.0, or 10 cc concentrated
acetic acid is added instead of acetone, the percentages of
sugar are 0.60, 0.70, and 1.06, respectively. The difference
between 1.04 and 1.06 would probably disappear if one cor-
rected for the effect of acetone and acetic acid upon the optical
rotation of sugar. In this case a moderate addition of acetone
or acetic acid cuts the adsorption of sugar down to zero.
On the other hand, Rona and Michaelis found that albumin
and acetone were each adsorbed by charcoal as though the
other were not there.

Lachs and Michaelis[3] found that caustic potash decreases
very much the adsorption of potassium chloride from water
by charcoal. In other words, the presence of the strongly ad-
sorbed hydroxyl ion decreases the adsorption of the chlorine
ion very much. They also find that the adsorption of chlorine
ion is increased markedly if sulphuric acid be added in small
amounts to a potassium chloride solution. This is in ac-
cordance with the results of Osaka[4] that potassium chloride is
adsorbed more strongly than potassium sulphate, sodium

[1] Chem. News, **17,** 217 (1896).
[2] Biochem. Zeit., **16,** 489 (1909).
[3] Zeit. Elektrochemie, **17,** 1 (1911).
[4] Mem. Coll. Sci. Kyoto, **1,** 267 (1915).

chloride than sodium sulphate, and presumably hydrochloric acid than sulphuric acid. We therefore get hydrochloric acid adsorbed and potassium sulphate left in solution.

I do not know of any record of experiments on the adsorption of mixtures of hydrogen and carbon monoxide by platinum; but I feel sure that carbon monoxide will be found to cut down the adsorption of hydrogen very markedly. It is to be hoped that somebody will try this experimentally.

Faraday found that ethylene decreased the catalytic action of platinum on hydrogen and oxygen more than did carbon monoxide; but this result is not confirmed by Henry[1] and probably was due to some impurity in Faraday's ethylene. "Olefiant gas, even when constituting one-fourth or one-third of the mixture, did not in the slightest degree retard the action of the platina balls or sponge. Several trials were made, in which the olefiant and explosive mixture were mingled in equal proportions. In all of these the ball acted instantaneously, and ascended rapidly in the tube during one or two minutes, when its rise was suddenly checked. Thus 1.02 cu. in. were reduced in the first minute to 0.90, and became 0.82 after an hour's contact. The following day only 0.56 was left, which was not diminished by washing with potassa. Even when the volume of the olefiant was double that of the explosion mixture, there was an instant action, though to less extent than in the last experiment. When the volume of the olefiant was three times that of the explosive mixture, no immediate action was visible, though a notable diminution always took place in the course of a few hours or on the following day. Finally, the activity of the black powder of Liebig was not suspended by the addition of twenty volumes of olefiant to one of explosive mixture.

"On subjecting to examination the gaseous products of these and other experiments on olefiant gas, mingled with various proportions of the explosive mixture, very different results from those afforded with carbonic oxide were obtained. In the greater number of experiments with olefiant gas, no

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[1] Phil. Mag., (3) **65**, 329 (1836).

appreciable diminution was caused by prolonged contact, or by subsequent washing with potassa; and though in some cases, when the explosive mixture considerably exceeded the olefiant, there *was* a perceptible absorption, yet the carbonic acid thus evidenced was always of small amount. In three successive experiments, in which olefiant gas and explosive mixture were mingled in equal proportions, there was no measurable product of carbonic acid. Yet in all these cases, though the ball ascended rapidly on first contact, its activity was soon suspended. Olefiant gas then possesses, like carbonic oxide, an undoubted power of retarding the union of hydrogen and oxygen, but it differs from carbonic oxide in not necessarily affording carbonic acid by so acting.

"Similar differences presented themselves on submitting mixtures of olefiant and oxygen only to the action of platina. To the observation of Dr. Faraday, 'that the most prolonged contact with the prepared plates never induced the union of the elements of olefiant with oxygen,' I may add, that the contact was not efficient, even when aided by the presence of liquid potassa. The spongy metal, similarly conjoined with potassa, was also for the most part entirely inert, and in the few instances in which carbonic acid appeared, it was formed very slowly, and in small quantity. At the temperature 490° Fahrenheit, however, the sponge has been shown to occasion the speedy though inexplosive combustion of olefiant in mixture with oxygen. Liebig's powder too caused the slow combination of the two gases at atmospheric temperatures, as was evidenced both by considerable diminution of volume, and by the test of lime-water; and when the tube containing the gaseous mixture and powder was surrounded with boiling water combination ensued with rapidity. Now the mode in which platina acts is of course identical in the various states of plate, sponge, or powder; the powder presenting only an infinitely larger extent of surface for gaseous contact than the plate or sponge. Hence the tendencies of the constituents of olefiant to unite with oxygen, which are evidenced by combinations to considerable amount in presence of the powder,

may be inferred to be operative, though less effectively, on the surface of the same metal under other forms; and viewed in connection with the unequivocal proofs of the nature of the interference of carbonic oxide, these tendencies may be admitted to furnish an adequate explanation of the more feeble interference of olefiant gas. The interfering power of carbonic oxide as respects the action of the platina balls is eighteen times as great as that of olefiant; carbonic oxide in the proportion of $^1/_{24}$th interfering as completely as olefiant in that of $^3/_4$ths of the mixture.

"The influence of temperature in quickening the action of the sponge or powder on mixtures of olefiant and oxygen strongly confirms this view, when taken in connection with a peculiarity observed in the mode of interference of olefiant gas. Thus it has been stated that olefiant mingled in equal bulk with explosive mixture did not prevent instant action; and that it began to interfere only when much of the oxygen and hydrogen had combined together, with the disengagement of great heat. The interfering power of olefiant gas, feeble at atmospheric temperatures, is then greatly augmented by heat, which had been already shown to determine the separate combination of the elements of olefiant with oxygen, and which is well known to exalt chemical affinity.

"In recapitulation, it may be stated that carbonic oxide interferes with the action of platina upon mixtures of oxygen and hydrogen, by virtue of its stronger affinity for oxygen, which causes it slowly to take the larger portion of that gas. Olefiant gas, which at common temperatures has a weaker attraction for oxygen than hydrogen, suspends the combining tendencies of those two gases, only when its volume greatly exceeds that of the mixture, in which case the weaker affinity is aided by a greater number of atoms. Even with this advantage olefiant is unable to appropriate the oxygen to itself, but only retards its union with hydrogen by opposing a weaker attractive tendency.

"Nor is the admission of attractive forces between the particles of mixed gases, even when not manifested by any

visible action (as between oxygen and the elements of olefiant gas), inconsistent with what is known of chemical affinity as operating in the solid and liquid forms of matter. In the eighth of his admirable series of memoirs on electro-chemistry, Dr. Faraday has shown that zinc, having its surface thinly amalgamated, though incapable, when immersed in dilute sulphuric acid, of effecting the decomposition of water, has yet the power, by its attraction for the oxygen of the particles of water in contact with its surface, to induce a peculiar state of electrical tension of polarity in those particles of water, as well as a similar but opposite state in the contiguous particles of zinc. By plunging a platina plate into the solution and completing the galvanic circle, this tension is relieved and decomposition of water instantly ensues. In the preparatory stage of the important experiment we have then a case of chemical forces in undoubted operation, yet giving no appreciable sign of their existence.

"Other arguments present themselves in favour of the opinion, that the property inherent in certain gases of preventing or retarding the union of hydrogen and oxygen is to be referred to their attraction for oxygen, and not to any peculiar action of the metallic surface, by which it becomes invested with the interfering gas. (1) All the gases which have been hitherto observed to exhibit this power, are such as are capable of uniting with oxygen; and the non-interfering gases are such as cannot, at least within a considerable range of temperature, be brought to combine with that element. (2) The property of interference follows, in its comparative energy, the same order as the respective combustibilities of the gases. Thus Sir Humphry Davy observed that carbonic oxide and olefiant were most inflammable, while carburetted hydrogen required for its combustion a much higher temperature, being neither fired by white-hot charcoal nor iron. Dr. Henry also has shown that in presence of the sponge, carbonic oxide combines rapidly with oxygen at from 300° to 340° Fahrenheit; olefiant at 520°; and carburetted hydrogen not at any temperature to which the mercurial bath

could be raised. I have ascertained that the two first gases observe the same order of union in presence of Liebig's powder, carbonic oxide inflaming at atmospheric temperatures, and olefiant gas being rapidly acted upon at $212°$. Now this progression is precisely that of their interfering powers, carbonic oxide acting when it constitutes only $1/_{24}$th of the mixture, olefiant gas not suspending action till it amounts to $3/_4$ths, and carburetted hydrogen possessing no power whatever of retarding the action of platina even when its volume exceeds by ten times that of the explosive mixture. Finally, that the restraining force is wholly dependent upon the relations of the mixed gases among one another, is deducible from the fact that the same gases which suspend the combining tendencies of hydrogen in presence of platina, resist also other modes of effectuating the union of those gases, for instance, the discharge of a Leyden jar. The curious facts observed by Professor Graham, respecting the power of even smaller quantities of the same and other gases to arrest the slow oxidation of phosphorus, are also favourable to the doctrine that the interfering gases act solely by virtue of their superior attraction for oxygen."

The relatively slight retarding action of ethylene is quite in accord with its presumably being adsorbed less strongly than hydrogen by platinum. If it only cuts down the adsorption of hydrogen appreciably when present in relatively large excess, it will have very little effect on the rate of combustion of oxyhydrogen mixtures. It is not possible to get satisfactory data as to the way in which platinum adsorbs mixtures of hydrogen and ethylene, because platinum causes these two gases to react.[1] It is not known to what extent this is a disturbing factor in Henry's experiments. It is quite natural under the circumstances that Henry should have drawn the conclusion that "the property inherent in certain gases of preventing or retarding the union of hydrogen and oxygen is to be referred to their attraction for oxygen and not to any peculiar action of the metallic surface by which it

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[1] Harbeck and Lunge: Zeit. anorg. Chem., 16, 34 (1898).

becomes invested with the interfering gas." That this is wrong can be seen from the fact that carbon monoxide is at least equally effective in checking the very different reaction between hydrogen and ethylene in presence of platinum. Here there is no oxygen and no oxidation and consequently the attraction of carbon monoxide for oxygen can play no part. The adsorption hypothesis explains both reactions equally well. If carbon monoxide cuts down the adsorption of hydrogen by platinum, it will interfere with the reaction between hydrogen and oxygen or ethylene. Henry's argument in regard to the respective combustibilities of hydrogen, carbon monoxide, ethylene, and methane holds only for certain conditions because under others methane and ethylene are burned more readily than either hydrogen or carbon monoxide.

Schönbein[1] pointed out that the hydrides of sulphur, selenium, phosphorus, arsenic, antimony, and tellurium act very energetically in cutting down the catalytic action of platinum on mixtures of air with hydrogen or ether. He is quite clear that the trouble is due to the formation of some sort of a film over the platinum and he considers the possibility that we may be dealing with a gas film of hydrogen sulphide, phosphide, etc. Schönbein rejects the assumption of a gas film on the ground that hydrogen sulphide, for instance, is more readily oxidized by oxygen than hydrogen and that consequently such a film would be destroyed at once. He therefore decides that the film is probably solid sulphur, phosphorus, selenium, arsenic, antimony, or tellurium, though he admits that this should be checked experimentally. I do not know whether Schönbein is right or not; but his reasoning is not necessarily sound. We have already seen that the combustion of mixed gases may proceed along very different lines in the presence and in the absence of a catalytic agent. It might be that hydrogen sulphide was adsorbed by platinum so much more strongly than its oxidation products that the platinum actually stabilized the hydrogen sulphide. This

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[1] Jour. prakt. Chem., **29**, 238 (1843).

is a question which should not be difficult to determine experimentally. The really important thing is that Schönbein saw so clearly that one must postulate the existence of a film of solid, liquid, or gas over the surface of the platinum if one is to account intelligibly for the poisoning of the platinum catalysis.

So far, all that I have done is to show that we can account for all the cases that have been considered if we postulate suitable and not improbable adsorptions. To make the case complete one ought to show that all substances which poison catalytic agents do cut down the adsorption of the essential reacting substance or reaction product.

One case involving a gas has been studied. Harbeck and Lunge[1] found that carbon monoxide prevents the catalytic action of platinum or palladium black on a mixture of ethylene and hydrogen. Special experiments showed that both platinum and palladium take up carbon monoxide and retain it pertinaciously. Lunge and Harbeck say that "both metals form compounds with carbon monoxide which are so stable that they must be considered as definite chemical compounds even though it is not possible to convert all the platinum or palladium into the corresponding compounds and to obtain them in a pure state for analysis. A purely mechanical adsorption of carbon monoxide is not probable because the carbon monoxide cannot be driven out by treatment with hydrogen or other gases. Also, after previous treatment with hydrogen the platinum takes up just as much carbon monoxide as without the treatment with hydrogen. Also it is only by assuming the existence of an actual chemical compound between Pt and CO that one can account for the fact that the contact action of platinum on a mixture of ethylene and hydrogen is checked so completely.

"The carbon monoxide is not set free until the platinum is heated to about 250° and then it comes off suddenly, which is also an argument for the existence of an actual chemical compound. These compounds of platinum and palladium are

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[1] Zeit. anorg. Chem., **16**, 50 (1898).

like those of carbon monoxide with nickel and iron. Since
they are not volatile nor soluble in the ordinary solvents, it is
not possible to isolate them or to decide upon their composi-
tions."

This was the proper view to take at the time when these
experiments were made; but, nowadays, it is clear that there
is no real evidence of the existence of a definite compound.
If the hypothetical compound is as stable as Lunge says,
there should be no difficulty in obtaining the compound in a
pure state. If this cannot be done—and Lunge's experiments
are not conclusive on this point—we must be considering a
case of adsorption. In any event the cutting down of the
catalytic action is due to the fact that the ethylene and hy-
drogen are not adsorbed to the same extent as when no car-
bon monoxide is present. Except from a theoretical point of
view, it is immaterial whether the platinum is coated with a
film of compound or with a film of adsorbed carbon monoxide.

Warburg[1] has found that at 38° oxalic acid is burned at
the surface of blood charcoal to carbon dioxide and water,
and that the reaction velocity is decreased by different nar-
cotics in a manner similar to the way in which they act on
the rate of oxidation in cells. "I first showed that charcoal,
which had been shaken with oxalic acid solution consumed
oxygen. When different kinds of charcoal were brought into
equilibrium with the same concentrations of oxalic acid, they
consumed very different amounts of oxygen. Merck's blood
charcoal used up the most oxygen and Kahlbaum's blood char-
coal somewhat less. There was no consumption of oxygen
when Kahlbaum's sugar charcoal was used. The different
charcoals show the same order with respect to adsorbing oxalic
acid. When equal amounts of charcoal were shaken for two
minutes with equal volumes of the same oxalic acid solution,
and the oxalic acid left in the solutions determined by titra-
tion, it was found that sugar charcoal had adsorbed practically
no acid, Kahlbaum's blood charcoal more, and Merck's blood
charcoal the most. Consequently, Merck's purest blood

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[1] Pflüger's Archiv., **155**, 547 (1913).

charcoal (purified with acid) was used in all experiments."

Methyl urethane in concentrations of 0.5–10.0 percent decreased the rate of oxidation 34–60 percent. With ethyl urethane the percentage decrease in reaction velocity was 42–76 for the same range of concentrations. Propyl urethane in concentrations of 0.05–5.0 percent decreased the reaction velocity 41–90 percent while phenyl urethane cut down the reaction velocity 90 percent when present in a concentration of only 0.05 percent. Similar results had previously been obtained for these same substances and the rate of oxidation in red blood cells.

Warburg expresses himself as follows in regard to the catalysis by charcoal and in regard to the poisoning of that catalysis: "That the combustion of oxalic acid takes place at the surface of the charcoal can scarcely be questioned; this is a typical case of surface catalysis. We do not know, however, in what way the conditions prevailing at the surface of the charcoal cause an increase in the rate of oxidation. It must be kept in mind that many substances, which are otherwise no more stable than oxalic acid, are concentrated at the surface of the charcoal but not burned. For instance, sugar is adsorbed but is not changed chemically.[1]

"There is one point that should not be overlooked. Merck's blood charcoal was used in my experiments and has often been used by others on account of its strong adsorbing power. Although this charcoal has been purified with acids, it nevertheless contains considerable inorganic matter,[2] including iron. It is easy enough to show this if one ignites the charcoal in the air. A light-colored ash is left which gives a strong test for iron. If one does not burn the charcoal but merely boils it with acid, only traces of iron go into the filtrate. Blood charcoal is by no means pure carbon but rather a combination of charcoal with inorganic constituents. The

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[1] Rona and Michaelis: Biochem. Zeit., **16**, 489 (1909).
[2] Ash determinations have been made by Glaessner and Suida: Liebig's Ann., **357,** 95 (1907).

iron content is especially noteworthy in view of the action of the charcoal in increasing the rate of oxidation.

"The most probable explanation for the retarding action is that the oxalic acid is displaced from the charcoal surface. In fact, each constituent of a mixture is always less strongly adsorbed than when it alone is in solution.[1] The more strongly adsorbed a substance is the more strongly it tends to displace another. The order of the different substances is therefore to be accounted for on the basis that more oxalic acid is displaced the more strongly the narcotic is adsorbed. Although the displacement of the oxalic acid by the adsorption of the narcotic is unquestionably the chief cause of the decrease in the rate of oxidation, I consider it very probable that this is not the only factor. I think that it is very probable that an important part is played by changes at the charcoal surface which do not depend on the displacement of the adsorption. If this hypothesis is right, one would expect that a narcotic would act similarly in all sorts of surface catalyses and with very different substrates."

Freundlich and Kaempfer[2] have studied an interesting case of the cutting down of adsorption in aqueous solution. Uranium X_1 is adsorbed strongly by charcoal and is displaced to some extent by very dilute solutions of thorium nitrate. The presence of a solution containing about .0.0004 millimol $Th(NO_3)_4$ (a little less than 0.2 mg. per liter) increases the concentration of uranium X_1 in the solution by about twenty percent. The charcoal is thus poisoned, so far as the adsorption of uranium X_1 is concerned, by infinitesimal amounts of thorium nitrate. When a stronger solution of thorium nitrate was used, the concentration of the uranium X_1 in the solution increased to over five-fold.

We have already seen that Henry increased the rate of reaction between carbon monoxide and oxygen in presence of platinum by adding caustic potash to remove the carbon

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[1] Michaelis and Rona: Biochem. Zeit., **15,** 209 (1908); Freundlich: "Kapillarchemie," 163 (1909).

[2] Zeit. phys. Chem., **90,** 681 (1915).

dioxide. It is easy to see that the piling up of the reaction products will cut down the reaction velocity if they prevent the reacting products from coming in contact with the catalytic agent. This has been observed in the contact sulphuric acid process.[1] The usual explanation is that we are dealing with diffusion only: but it is more likely that there is a cutting down of the adsorption, since this is the most important factor when carbon monoxide poisons platinum with reference to the hydrogen-ethylene reaction. A special case of some interest is the reaction between carbon monoxide and oxygen at about 300° with quartz glass as catalytic agent.[2] "Oxygen acts at any rate qualitatively about as it should, the rate of reaction increasing with increasing concentration. Carbon monoxide behaves quite differently and tends to check its own combustion under these circumstances. It is a negative autocatalytic agent. In all the experiments the peculiar result was obtained, that the absolute reaction velocity increases with decreasing concentration of carbon monoxide and decreases with increasing concentration." Bodenstein offers no explanation for this surprising result though he calls attention to the fact that carbon monoxide acts as a poison in many cases. There are no data in regard to the adsorption of carbon monoxide by quartz glass from which one could predict the results obtained by Bodenstein and Ohlmer; but if carbon monoxide displaces oxygen sufficiently at the surface of the catalytic agent, one would get exactly the results that Bodenstein and Ohlmer found experimentally. It is therefore probable that the action of carbon monoxide in poisoning its own combustion with oxygen is due to its displacement of oxygen from the adsorption film. When discussing the fractional combustion of carbon monoxide and hydrogen in presence of platinum, stress was laid on the fact that carbon monoxide must cut down the adsorption of hydrogen by platinum. It is also possible that carbon monoxide

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[1] Bodenstein: Zeit. Elektrochemie, **9,** 696 (1903); Berl: Zeit. anorg. Chem., **44,** 267 (1905).

[2] Bodenstein and Ohlmer: Zeit. phys. Chem., **53,** 166 (1905).

cuts down the adsorption of oxygen by platinum though this cannot be the important factor because carbon monoxide also poisons the reaction between hydrogen and ethylene in presence of platinum.

A case which has been studied a great deal quantitatively is the decomposition of hydrogen peroxide solution by platinum. One of the most interesting things about this reaction is its extreme sensitiveness to the so-called poisons.[1] The rate of decomposition of hydrogen peroxide by a given solution of colloidal platinum was reduced approximately to one-half by $M/20\ 000\ 000$ HCN, $N/2\ 000\ 000$ $HgCl_2$, and $N/300\ 000$ H_2S. Curiously enough it had been shown by Schönbein[2] that these same substances cut down the catalytic action of red blood corpuscles on hydrogen peroxide. Owing to the similarity between the action of colloidal metals and organic ferments in many cases Bredig called the colloidal metals prepared by his method inorganic ferments. This stirred up a violent discussion because people seemed to think that the colloidal metals ought to behave exactly like the ferments in every respect or ought not to behave like them at all. In Table I are given data[3] for the concentration necessary to cut down the rate of decomposition of hydrogen peroxide to one-half when the catalytic agents are colloidal platinum and haemase, the active enzyme in the red blood corpuscles. While many of the substances that cut down the platinum catalysis also decrease the catalytic action of haemase, there are many cases where no parallelism occurs. Thus carbon monoxide is very toxic to platinum and has no effect on haemase. On the other hand nitric acid, sulphuric acid, and potassium chlorate have practically no effect on platinum and are quite toxic to haemase. Even where there is a general parallelism, one must not follow it too closely. With platinum the prussic acid solution has one-tenth the concentration of the mercuric

[1] Bredig and von Berneck: Zeit. phys. Chem., **31**, 258 (1899); Bredig and Ikeda: Ibid., **27**, 1 (1901).

[2] Jour. prakt. Chem., **105**, 202 (1868).

[3] Senter: Zeit. phys. Chem., **51**, 701 (1905).

TABLE I

Concentrations at which poisons reduce the rate of the catalytic
decomposition of hydrogen peroxide approximately to
one-half

Poison	Colloidal platinum	Haemase
H_2S	M/300 000	M/1 000 000
HCN	M/20 000 000	M/1 000 000
$HgCl_2$	M/2 000 000	M/2 000 000
$HgBr_2$	——	M/300 000
$Hg(CN)_2$	M/200 000	M/300 000
I_2 in KI	M/5 000 000	M/50 000
$NH_2OH.HCl$	M/25 000	M/80 000
Phenyl hydrazine	——	M/20 000
Aniline	M/5000	M/400
Arsenious acid	M/50	No poisoning at M/2000
CO	Very poisonous	No poisoning
HCl	M/3000	M/100 000
NH_4Cl	M/200	M/1000
HNO_3	No poisoning	M/250 000
H_2SO_4	No poisoning	M/50 000
KNO_3	No poisoning	M/40 000 at $0°$
$KClO_3$	Slight poisoning?	M/40 000 at $0°$

chloride solution while with haemase it has double the con-
centration. The tabulated concentration for mercuric
chloride is the same for platinum as for haemase, while that
for iodine dissolved in potassium iodide is one hundred times
as great for haemase as for platinum. Kastle and Loevenhart[1]
point out that prussic acid is a strong poison for colloidal plat-
inum and colloidal silver but accelerates the catalysis of
hydrogen peroxide by iron and copper. The whole matter
becomes a good deal clearer if we consider that the so-called
poisons are adsorbed strongly by the catalytic agent and there-
fore prevent or decrease the adsorption of hydrogen peroxide.[2]
This adsorption will be specific and will therefore in general
not be the same quantitatively for different catalytic agents.
On the other hand there may well be a qualitative agreement

[1] Am. Chem. Jour., **29**, 397 (1903).
[2] Cf. Senter: Zeit. phys. Chem., **51**, 702 (1905); Denham: Ibid., **72**,
689 (1910).

in some or even in many cases, which is exactly what is found
experimentally. Owing to the extreme flexibility of this
hypothesis there is nothing as yet to prevent its accounting
for all the phenomena observed.[1] On the other hand it must
be remembered that proof is still lacking that platinum adsorbs
prussic acid, for instance, much more strongly from an aqueous
solution than it does hydrogen sulphide or that there is no
such difference with haemase. It is also to be remembered
that there is no experimental proof as yet that platinum ad-
sorbs the poisons strongly. We do know, however, that many
of the substances that poison the platinum catalysis of hy-
drogen peroxide also poison the platinum catalysis of oxy-
hydrogen gas. In fact Ernst[2] arranges the substances which
he studied in the following order in regard to their poisoning
action on the platinum catalysis of oxyhydrogen gas, the
strongest poison coming first: prussic acid, cyanogen iodide,
alkaline sodium thiosulphate, mercuric chloride, hydrogen
sulphide, iodine, bromine phosphine, hydroxylamine hydro-
chloride, mercuric cyanide, hydrazine sulphate, arsenious acid,
phenol. Ernst points out that this is also the order in which
the substances poison the platinum catalysis of hydrogen
peroxide. Although a ten percent solution of formic acid pre-
cipitates colloidal platinum, it increases the rate of reaction
of oxyhydrogen gas three-fold. Ernst cites Ikeda as his
authority for stating that formic acid has a similar effect on
the platinum catalysis of hydrogen peroxide.

   Meyerhof[3] has shown that the alcohols and the urethanes
act as poisons for the catalytic decomposition of hydrogen
peroxide by platinum. He examined the solution with the
ultramicroscope and found that addition of these poisons—
or narcotics, as he prefers to call them—caused no, or prac-
tically no, decrease in the number of visible particles. He
concludes that the decreased rate of decomposition in presence
of poisons is not necessarily due to an agglomeration of the

[1] Cf. Freundlich and Kaempfer: Zeit. phys. Chem., 90, 681 (1915).
[2] Zeit. phys. Chem., 37, 483 (1901).
[3] Pflüger's Archiv., 157, 307 (1914).

platinum. Meyerhof considers it probable that the strongly adsorbed narcotic forms a film over the surface of the catalytic agent which prevents the reacting substance from coming in contact with the catalytic agent. Meyerhof[1] has also shown that the alcohols and the urethanes cut down the rate at which invertase inverts sugar. He concludes very properly that this is due to the displacement of the sugar from the surface of the colloidal invertase.

There may be other factors which must be taken into account. Thus Bredig[2] points out that when colloidal platinum is allowed to stand in contact with hydrogen peroxide and concentrated potassium cyanide, the platinum flocculates and precipitates. The agglomerated platinum causes the hydrogen peroxide to decompose, thus showing that the cyanide does not poison precipitated platinum black. There seem to be only two possible explanations. One is that the adsorption of potassium cyanide by platinum falls off very much more rapidly with increasing size of the platinum particles than does the adsorption of hydrogen peroxide by platinum. The other explanation is that, through oxidation or otherwise, there is formed what might be called an anti-body, which cuts down the adsorption of the cyanide. Neither hypothesis is very satisfactory and neither is supported by any experimental evidence that I know of except that Jablczynski[3] found that platinized platinum decomposes hydrogen peroxide one hundred times as fast and chromous chloride only three times as fast as does smooth platinum foil. The matter should be taken up because Rosnyak[4] claims that the catalytic action of platinum on hydrogen peroxide increases with increasing dispersity while Felgate[5] states that pulverulent nickel reduces nitric oxide and colloidal nickel does not. In both cases it is probable that some factor has been overlooked or not stated.

Pflüger's Archiv., **157**, 251 (1914).
Zeit. phys. Chem., **31**, 332 (1899).
Ibid., **64**, 751 (1908).
Ibid., **85**, 68 (1913).
Chem. News, **108**, 178 (1913).

The more finely divided the platinum the more likely the
surface is to be coated with oxide and it does not follow at all
that the catalytic action of metallic platinum is the same as
that of an oxide of platinum. If the metal is kept in sus-
pension by means of gelatine or some similar substance, this
will have an effect on the adsorption and consequently on the
catalytic agent. The increase in stability of the colloidal
metal may have to be paid for in a decreased catalytic action.

As a result of the hypothesis developed in this paper it is
now possible to offer a plausible explanation of some electro-
lytic phenomena which have been most puzzling hitherto.[1]
"It is very remarkable that the rise of potential at a smooth
platinum anode is sometimes dependent on the nature of the
electrolyte. The difference of potential between smooth and
platinized platinum is less in sulphuric acid than in caustic
soda, other conditions being the same. A slight addition of
hydrofluoric acid to sulphuric acid increases the potential at
which oxygen is set free at smooth platinum by an amount
varying from several hundredths of a volt to a tenth of a volt
provided the temperature is low and the current density not too
high. The increase in potential is greater the ratio of hydro-
fluoric acid to sulphuric acid and reaches a maximum for pure
hydrofluoric acid.[2] Hydrochloric and hydrobromic acids
behave similarly except that with these acids the maximum
potential is reached with slight additions so that the amount
of the halide acid is only a few percent of the total acid con-
centration. Here also the potential in pure hydrochloric acid
is higher than in an equivalent sulphuric acid solution in case a
sufficient evolution of oxygen is provided by keeping the con-
centration of the hydrochloric acid sufficiently low and the
current density sufficiently high. In normal HCl a current
density of 0.057 amp/cm² is sufficient.[3] Nitric acid is very
variable. In normal acid solution it always raises the poten-
tial; but in a 10 N acid solution the addition of a small amount

[1] Foerster: "Elektrochemie wässeriger Lösungen," 284, 735 (1915).

[2] Müller: Zeit. Elektrochemie, 10, 780 (1904).

[3] Müller and Scheller: Zeit. anorg. Chem., 48, 112 (1905).

of acid raises the potential whereas addition of more nitric acid lowers it a good deal, so much so that between 10 N H_2SO_4 and 10 N HNO_3 the potential for the evolution of oxygen[1] falls 0.28–0.65 volt for anode current densities of 0.05–0.5 amp/cm^2 and a temperature of 12°. In caustic soda solution presence of NO_3' raises the anode potential. Ammonia has the same effect because it is oxidized at the anode to nitrate.[2]

"It is very often customary to use platinum black as a means of accelerating the oxidizing action of atmospheric oxygen. Oxidations which take place readily at a platinized anode may therefore be considered as being accelerated catalytically by the platinum black of the anode. The power of platinum black to act catalytically in oxidations and in many other chemical reactions is affected very markedly by certain substances, such as prussic acid, mercuric cyanide, etc.[3] The same substances have a similar action on many electrolytic oxidations occurring at platinized anodes; they cut down the rate of oxidation and when the current or the rate of oxidation is kept constant, cause an increase of the anode potential which gives a higher oxygen pressure in the solution and therefore restores the old reaction velocity. When a solution of sodium thiosulphate is kept absolutely neutral, it is oxidized quantitatively to tetrathionate[4] at a platinized anode with a potential of + 0.44 volt for a current density of 3.10^{-4} amp/$cm.^2$ If one adds a trace of mercuric cyanide the anode potential at which the same current is obtained rises to + 0.48 volt. From this it follows that the oxidation process really takes place through an intermediate formation of oxygen according to the reaction

$$2S_2O_3'' + O + H_2O \longrightarrow S_4O_6'' + 2OH'$$
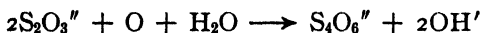
[1] Schellhaass: Zeit. Elektrochemie, **14,** 121 (1908).

[2] Müller and Spitzer: Ibid., **11,** 920 (1905).

[3] Bredig and von Berneck: Zeit. phys. Chem., **31,** 324 (1899); Bredig and Ikeda: Ibid., **37,** 1 (1901).

[4] Thatcher: Ibid., **47,** 693 (1904). It is still an open question to what an extent in these and similar cases the action of the retarding substances may or may not be due to the formation of thin diaphragms.

and not, as one might have expected, according to the reaction

$$2S_2O_3'' + 2F \longrightarrow S_4O_6^{-''}.$$

In addition to these essentially catalytic actions of certain dissolved substances which are not used up during the electrolysis, there are some other remarkable phenomena which are distinctly different in nature.   When discussing the anodic evolution of oxygen we became acquainted with the surprising and still unexplained fact that certain anions, such as Cl', F', SO_4'', ClO_4'', etc., increase markedly the anode potential at which oxygen is evolved at a smooth platinum anode. The presence of substances which increase the anode potential aids such anodic oxidations as call for a high anode potential. Thus the current yield of persulphates is increased by the addition of small amounts of hydrochloric acid,[1] which increase the anode potential.[2]   The oxidation of iodate to periodate does not take place in neutral solution at a smooth platinum anode, but takes place readily if the solution contains chloride, chlorate, or sulphate in addition to iodate.[3] The electrolysis of acetates at smooth platinum gives rise chiefly to ethane and carbon dioxide; but the products are chiefly methyl alcohol and carbon monoxide [?] when the acetate solution contains chlorate, sulphate or bicarbonate.[4] Fluoride ions are especially active; they increase the oxidation of chromic sulphate to chromic acid or of manganous sulphate to permanganic acid.[5]   In the electrolysis of potassium iodate, addition of fluorides causes an increase in the current yield of periodate from zero up to 30 percent;[6] in the electrolysis of potassium sulphate addition of fluorides increases the yield from 50 percent to 80 percent.[7]   In these last cases the fluorine anions cause a marked increase in the anode potential.   In the instances of electrolytic reduction there is nothing comparable to this group of phenomena."

[1] Elbs and Schönherr: Zeit. Elektrochemie, **2,** 250 (1895).

[2] Müller and Scheller: Zeit. anorg. Chem., **48,** 112 (1905).

[3] Müller: Zeit. Elektrochemie, **7,** 516 (1901); **10,** 64 (1904).

[4] Hofer and Moest: Liebig's Ann., **323,** 284 (1902).

[5] Skirrow: Zeit. anorg. Chem., **33,** 25 (1903).

[6] Müller: Zeit. Elektrochemie, **10,** 753 (1904).

[7] Müller: Ibid., **10,** 776 (1904).

Foerster seems to distinguish between the mercuric cyanide on the one hand and the fluoride ions on the other, calling the action of the first catalytic and the action of the second something else. There is a distinction between the two sets of substances; but it is not the one that Foerster makes. It is true that when one is using chlorine ion to raise the anode potential, there may be a change in this ion. Thus Müller[1] points out that when iodate is electrolyzed in presence of chloride, the process at the anode may consist chiefly in the formation of chlorine or hypochlorous acid and that these then react chemically to oxidize the iodate to periodate. While this may perhaps happen with chlorides, it certainly does not happen with fluorides. The essential part of the action is therefore catalytic, the fluoride remaining unchanged at the end of the run. As I see it, the two substances, mercuric cyanide and potassium fluoride, both act as poisons but they poison different reactions. The mercuric cyanide cuts down the adsorption of thiosulphate and therefore decreases the oxidation and increases the polarization. To get the same current one must increase the voltage. There is no evidence in Thatcher's experiments that mercuric cyanide increases the over-voltage at the anode and Foerster assumes that it does not. In the case of potassium fluoride we do have an increase in the over-voltage, which means therefore an increase in the monatomic oxygen. If potassium fluoride poisons the anode for the reaction $2O \longrightarrow O_2$, it would produce just the effects which we actually get and this is therefore a satisfactory working hypothesis for the time being. Whether it actually does retard this reaction is a matter to be tested experimentally. We ought to find a distinct relation between the substances which poison the hydrogen peroxide catalysis and those which change the over-voltage of a platinum anode.

Foerster says that we have nothing equivalent to this at the cathode; but I think that that is merely because we have not looked for it. There is only a very slight over-voltage with a smooth platinum cathode in sulphuric acid solution.

[1] Zeit. Elektrochemie, **10**, 753 (1904).

There is a very large over-voltage with smooth platinum in a cadmium sulphate solution. It seems to me probable that one could get any intermediate value by taking a suitable mixture of cadmium sulphate and sulphuric acid or zinc sulphate and sulphuric acid. Nobody has ever tried this consciously because there was no especial reason for doing it, though the addition of a copper salt in the electrolytic determination of nitric acid is very possibly a case in point where the thing was done empirically.

The general conclusions to be drawn from this paper are:

1. Since contact catalysis involves adsorption, a decrease in the adsorption will mean a decrease in the reaction velocity, other things remaining the same.

2. The adsorption may be decreased by the presence on the solid catalytic agent of a film of solid, liquid, or gas.

3. Very small amounts of grease will keep palladium from taking up hydrogen.

4. Carbon monoxide cuts down the catalytic action of platinum on oxyhydrogen gas and is itself oxidized slowly.

5. The preferential oxidation of carbon monoxide is not the reason for its poisoning the catalytic action of platinum on oxyhydrogen gas.

6. Carbon monoxide is retained tenaciously by platinum and carbon monoxide practically destroys the catalytic action of platinum on hydrogen and ethylene.   .

7. Carbon monoxide undoubtedly decreases the adsorption of hydrogen and ethylene by platinum though there are no direct measurements to show this.

8. Since the presence of the reaction products will decrease the rate at which the reacting substances will diffuse to the catalytic agent and since the reaction products may decrease the adsorption of the reacting substances, the reaction products may decrease the reaction velocity if they are not removed.

9. The reaction between carbon monoxide and oxygen in presence of platinum is accelerated by the addition of caustic potash to remove the carbon dioxide.

10. Sulphur trioxide decreases the rate at which sulphur dioxide and oxygen react.

11. If one reacting substance decreases the adsorption of the other very much, presence of an excess of the first may decrease the reaction velocity.

12. When a mixture of carbon monoxide and oxygen is catalyzed by quartz glass, an increase in the concentration of the oxygen increases the reaction velocity but an increase in the concentration of the carbon monoxide decreases it.

13. Since the poisoning of the hydrogen peroxide catalysis is due to selective adsorption there is no necessary reason why the same substances should poison both platinum and haemase or should poison them to the same extent.   On the other hand, there is no reason why there should not be a certain parallelism and that is all that actually occurs.

14. When a colloidal metal is kept in suspension by the addition of gelatine or other substance, the stabilizer may cut down the adsorption and consequently may tend to decrease the reaction velocity.

15. If the retarding effect due to the stabilizer is greater than the accelerating effect due to increased surface, a stabilized colloidal metal may be less effective than a pulverulent metal which is not handicapped by a stabilizer.

16. The action of mercuric cyanide, etc., in cutting down the electrolytic oxidation of thiosulphate is probably due in part to its decreasing the adsorption of thiosulphate at the anode.

17. The action of fluoride ions, etc., in increasing the anode over-voltage is undoubtedly due to the fact that they decrease the catalytic action of the anode on the reaction $2O \longrightarrow O_2$.

18. An increase in over-voltage at the cathode could undoubtedly be obtained by taking a suitably acidified solution of zinc sulphate or cadmium sulphate.   It is possible that the addition of copper salts in the electrolytic determination of nitrates is analogous to the addition of chlorides or fluorides in the electrolytic formation of persulphates.

Cornell University

THE MORDANTING ACTION OF METALLIC FERRO- AND FERRICYANIDES[1]

BY ARTHUR B. CLARK

There has been very little quantitative work done on the mordanting action of metallic salts, probably because workers were in search of a specific result and performed only the experiments which seemed most likely to be successful.

The mordanting action is a function of the nature of the dye, and of the acid and metal united in the mordant, and also probably of the concentration of the ions in the solutions. In some cases there is possibly an effect of exposure to light, *e. g.*, in the silver compounds. As in any dyeing process, the concentration of hydrogen and hydroxyl ions and neutral salt has a very great influence on the result.

With this large number of factors it is easy to understand the contradictory results which have been obtained. These results are also very greatly affected by the physical state of the mordant, *i. e.*, colloidal or crystalline, and are very much complicated in case the mordant is in gelatine. In order to simplify the problem, the experiments described were conducted in a system containing only water, the mordant, the inorganic salt resulting from the action of the soluble metal and acid salts, the dyestuff, and a slight excess of acid salt to insure uniformity. A control series was run in the case of silver ferrocyanide to determine the effect of the presence and nature of the neutral salt.

Ferri- and ferrocyanides of the heavy metals were chosen for the experiments and the mordanting action of the following ferro- and ferricyanides was studied; cuprous, cupric, silver, zinc, cadmium, mercurous, mercuric, cerous, ceric, thorium, stannous, stannic, lead, vanadium, bismuth, uranyl, manganous, ferrous, ferric, cobaltous and nickelous. The dyes were selected to represent the common groups from the standpoint of chemical classification and a few more were included to represent special characteristics of the organic molecule. The dyes chosen were:

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[1] Communication No. 46 from the Research Laboratory of the Eastman Kodak Company.

TABLE I

No.	Name	Constitution	Characteristic
1	Sulphanilic acid coupled with Neville and Winther acid (sodium salt)	Oxy-azo	acid
2	Tartrazine	Pyrazolone (disazo carboxy)	acid
3	Fuchsine	Triphenyl-methane-triamine	basic
4	Crystal Violet	Triphenyl-methane-hexamethyltriamine	basic
5	Acid Violet 4 BC	Triphenyl-methane acid-tridialkyl-amine	acid
6	Rose Bengal	Fluorescein (halogenated)	acid
7	Acridine Orange NO	Amino-acridine	basic
8	Alizarine Red S	Sulpho-alizarine	acid
9	Tanninheliotrope	Methylamino-azine	basic
10	Capri Blue GON	Alkylamino-oxazine	basic
11	Methylene Blue BB	Alkylamino-thiazine	basic
12	Quinoline Yellow	Disulfo-phthalo-quinaldine	acid

Crystal Violet and Acid Violet 4 BC were taken because they represent basic and acid alkylated aminotriphenyl methane dyes. Rose Bengal is an acid dye containing a so-called "basic oxygen" atom.

Since a 5% excess of the acid salts was used, the effect of a large excess of these salts on the dyes was determined. The effect was in most cases inappreciable, and for the one exception noted, in the table, it was assumed that the slight action of a 5% excess would not influence the results.

TABLE II

Action of large excess of potassium ferrocyanide and potassium ferricyanide on the dyes

		Ferro-cyanide	Ferricyanide
1	Benzenesulphonic-azo N. and W. salt	nil	nil
2	Tartrazine	nil	nil
3	Fuchsine	nil	yellow and vvs. ppte.
4	Crystal Violet	nil	redder
5	Acid Violet 4BC	nil	redder
6	Rose Bengal	nil	yellower
7	Acridine Orange NO	nil	vs. ppte.
8	Alizarine Red S	nil	yellower
9	Tanninheliotrope	nil	yellower
10	Capri Blue GON	nil	greener
11	Methylene Blue BB	nil	partially pptd.
12	Quinoline Yellow	nil	nil

The method of testing the mordanting power consisted in the preparation of a suspension of the insoluble ferri- or ferrocyanide of such molar concentrations as to show clearly the relative mordanting action on the various dyes. This concentration was usually 0.005 M but in several cases other concentrations were used for obvious reasons. About 20 cc. were treated in a test tube with three drops of a 5% solution of the dyes selected and the amount of dye in solution after the precipitate settled out roughly determined by comparison with standards.[1]

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[1] The tabulation of the experimental data is omitted in order that the presentation may be more concise. It is believed that the tables and conclusions given contain all the data of interest.

Copper Salts

Ferricyanide mordants better than ferrocyanide and cupric better than cuprous. Cupric ferricyanide distinctly mordants the basic dyes better than the acid. Cuprous ferricyanide is selective, but in general it mordants the basic dyes better than the acid dyes.

Silver Salts

Silver ferricyanide is a selective mordant for basic dyes as is also the ferrocyanide but is more pronounced in its action. The washed ferrocyanide shows practically the same action as that in excess ferrocyanide, the washed mordant being slightly less active; but in presence of excess of silver ions, there is a pronounced difference. The acid dyes are very completely mordanted, this being the case with only a few of the mordants. This action is not due to the formation of the silver-dye salt because in a comparison series containing only silver ions and dye there was no measurable loss of dye by precipitation of the silver salt. However, the presence of the silver ion tends to cause precipitation of the acid dyes as the presence of excess anion favors the precipitation of the basic dyes.

The silver ferrocyanide turns blue under a white top layer on standing in the test tube. Since silver ferrocyanide is commonly described as being unaffected by light, this discoloration may be due to a trace of adsorbed silver nitrate or silver chloride.

Zinc Salts

The zinc salts are remarkable in that they exhibit the strongest mordanting power of any of the metal salts. The ferricyanide especially has about ten times the mordanting power of the other metal ferricyanides. An explanation may be a difference in physical state; that is, assuming that the precipitate is much more finely divided, it is to be expected that the dyes would be much more strongly adsorbed than by coarser particles. The zinc salts mordant quinoline yellow

showing that they have much greater mordanting power than the other metal salts.

Cadmium Salts

Although cadmium is chemically very closely allied to zinc, it has not the same mordanting power, indeed the cadmium salts are, with two exceptions to be noted later, the poorest of the mordants, the ferricyanide being the better of the two.

Mercury Salts

The mercurous ferricyanide is an excellent mordant for the basic dyes but the precipitate is only slightly colored, indicating that the dye may be chemically affected as is the case with mercuric ferricyanide. The action of the mercury salts is more pronounced on basic dyes than on the acid dyes.

Cerium Salts

Of the cerium salts, ceric ferricyanide precipitates or destroys nearly all of the dyes. The cerous salts are not of special interest, the ferricyanide not producing precipitates.

Thorium Salts

The ferricyanide mordants the basic dyes but the ferrocyanide seems to be a specific mordant for acid dyes. Since thorium ferrocyanide exhibited a strong specific adsorptive power on acid dyes, its action on nearly one hundred and fifty acid dyes was determined in comparison with aluminum chloride, the latter on 1% solutions of the dyes. It was hoped that it would be found a more valuable specific mordant than the aluminum chloride but a few dyes were precipitated by aluminum chloride which were not mordanted from their dilute solutions by the thorium salt. Thus the only practical value of the test would be in cases where only a small amount of dye is available.

Tin and Lead Salts

The tin and lead salts do not exhibit any striking characteristics, the ferricyanides being more active than the ferrocyanides.

Vanadium Salts

The vanadium salts show colloidal precipitation but the results are not conclusive as the only vanadium salt available was one containing a small amount of oxalic acid.

Bismuth Salts

In order to prevent the formation of the oxy bismuth salts, a small amount of hydrochloric acid was added to the solution. The salts are mordants for basic dyes, the ferricyanide being the better.

Uranium Salts

The uranium salts show strong mordanting action especially for basic dyes, the action of the ferricyanide being slightly more pronounced.

Manganese, Iron, Nickel and Cobalt Salts

The mordanting action of these salts is on the whole comparatively slight. The action is greatest on the complex acid dyes and especially on Alizarine which is in accord with dyeing practice in which salts of these metals are used as mordants. It is remarkable that the ferrocyanide of nickel, otherwise a weak mordanting agent, should mordant quinoline yellow to a slight extent.

Silver Halides

The outstanding fact concerning the halogen silver salts is that the mordanting power is very slight. The iodide is the only one which shows effective mordanting, and that only at a concentration three times that used for the other metals.

The numerical tabulation of results is given below. The action is scaled as follows on the basis of o.oo5 M suspensions.

imperceptible	1
very slight	2
slight	3
pronounced	5
nearly complete	7
complete	10

Arthur B. Clark

TABLE III

Metals	Acid Dyes		Basic Dyes		Size of Molecule	
	Ferricyanide	Ferrocyanide	Ferricyanide	Ferrocyanide	Ferricyanide	Ferrocyanide
Cuprous	3	1	5	1	402	465
Cupric	4	3	10	2	680	335
Silver (excess cyanide ion)	5	5	10	7	535	630
Silver (excess silver ion)	—	15	—	5	—	—
Silver (washed)	—	5	100	7	—	—
Zinc	8	5	—	7	619	350
Cadmium	2	2	3	2	760	435
Mercurous	7	3	10	10	815	1012
Mercuric	—	5	—	7	1027	812
Cerous	3	5	5	5	352	1200
Ceric	15	3	—	7	1268	350
Thorium	10	20	10	2	1544	440
Stannous	3	.5	7	7	780	450
Stannic	5	2	10	3	1205	330
Lead	3	3	10	1	1220	630
Vanadium	3	2	10	—	263	836
Bismuth	5	5	10	7	420	1465
Uranyl	5	5	7	5	483	1710
Manganous	1	2	3	2	589	300
Ferrous	1	2	2	2	600	320
Ferric	—	3	—	2	—	860
Cobaltous	2	3	2	2	600	320
Nickelous	2	5	2	1	611	330
Silver chloride	—	0	—	0	140	Halides
Silver bromide	—	0	—	1	190	—
Silver iodide	—	1	—	2	235	

The average mordanting power of each metal (obtained from the table) if placed in the periodic table instead of the atomic weight shows ·a systematic relation between mordanting power and position in the table. The high valent high atomic weight metals form ferro- and ferricyanides whose mordanting power is very great. The irregularities are probably due to difference in physical state of subdivision which enters as a secondary effect.

<div align="center">

TABLE IV

Periodic Classification

</div>

Na	Mg	Al	C		N		O	F	
Cu	Zn			V	Cr	Mn	Fe	Ni	Co
6	30			5		2	2	2	2
Ag	Cd		Sn						
8	2		6						
	Hg	Ce	Pb	Bi					
	8	6	5	7					
		Th			U				
		10			6				

Conclusion

Three general conclusions may be drawn:

(1) All ferricyanides mordant basic dyes better than acid dyes in the presence of a slight excess of ferricyanide ion.

(2) All ferrocyanides with the exception of thorium and lead mordant basic dyes in the presence of excess ferrocyanide ion. In the case of lead there is the possibility of the presence of a basic salt which would explain the abnormality. In the case of thorium the high molecular weight of the ferrocyanide may be the explanation, though it is probable that the presence of the heavy multivalent ion (which tends to precipitate the acid dyes) is the more logical explanation.

(3) Ferricyanides mordant better than ferrocyanides. On inspection of the table of relative mordanting powers, the metals are seen to fall into certain natural groups.

I. Manganese, cobalt, iron, nickel and the silver halides show practically no mordanting action. The explanation in the case of the halides is possibly the low molecular weight;

if equal weights of the iodide and ferrocyanide were taken, the action would probably be of the same order of magnitude, but the bromide and chloride would still be abnormally inactive.

II. Cadmium, cuprous, cerous, stannous and

III. Cupric, stannic, lead, vanadium, bismuth, uranium and ceric form intermediate classes.

IV. The heavier metals silver, mercury and thorium are the strongest mordants.

An attempt to connect the mordanting power with the molecular weight of the mordant is only partially successful. That there is such a definite connection is indicated by the extremely light (silver halide) and extremely heavy (cerium, thorium, tin, lead, bismuth, uranium) molecules but this is at least partially masked by the physical state. It is practically the same method of expression as the periodic system.

The work has shown definitely that mordanting power in the presence of slight excess of cyanogen compound is primarily a function of the molecular weight and valence of the metals. Secondary factors are the physical state of subdivision and molecular weight of the mordant. It is probable that the nature of the adsorption complex varies in most cases with the ionic concentration in solutions.

NEW BOOKS

Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry. *Vol. I (1916). 21 × 15 cm; pp. 335. London: Harrison & Sons, 1917. Price: 5/6.*—This is the first volume of what should be a very valuable series of annual reports on progress in applied chemistry. The volume does not cover the whole ground because the compilers of the sections on fibers, dyeing, metallurgy, electrochemistry and sugar were unable to finish their manuscripts in time. For obvious reasons no report on explosives will be made for the present. The separate articles are entitled: fuel and heating; gas—destructive distillation—tar products; mineral oils; coloring matters and dyes; acids, alkalies, salts, etc.; glass and ceramics; building materials; oils, fats, and waxes; paints, pigments, varnishes, and resins; india-rubber, etc., leather and glue; fermentation industries; water purification and sanitation; fine chemicals; medicinal substances, and essential oils; photographic materials and processes.

There is an interesting paragraph on the low temperature distillation of coal, p. 39. "Probably in no other department of the industry is research so much required as upon this question of distillation at low temperatures, and an investigation of this nature would profit by the experience of the gas engineer and chemist. A perusal of recent gas literature creates an impression that the proposition is generally received with antipathy. This attitude may have arisen as a result of the failure of earlier attempts promoted too exclusively by the financier. The fact remains, however, that raw coal should be treated, prior to its use for industrial and domestic purposes, for the extraction of valuable carbonaceous compounds, ammonia and sulphur. The richer hydrocarbons produced during the combustion of coal which are recovered by this process cannot, in most cases, be adequately utilized in existing appliances, and disappear as smoke. The adoption of such a process may solve the problem of the shortage of ammonia in the United Kingdom. An investigation of this nature is one which gas engineers and chemists are eminently competent to undertake, and, moreover, the interests of gas undertakings as purveyors of gaseous fuel need not be affected by the additional responsibility of preparing solid fuel; in fact, in the combination of the two processes appears to lie the ultimate scientific solution of the problem."

On p. 53 there is a brief discussion of the coking property of coal. "The property in coal of forming coke appears to depend upon the presence of constituents which melt at a lower temperature than that at which the rate of decomposition or carbonization becomes rapid. Certain of these constituents are readily oxidized, and this property is considered to account for the fact that the coking property of coals is diminished by exposure to air. By heating coal in an inert atmosphere for several hours at 300° C, the coking power of some coals is destroyed and of others weakened. The true coking coals appear to retain sufficient resin-like bodies after being heated to about 300° C to yield the necessary fusible material to form coke when heated to 320° C or above. Feebly coking coals yield a similar fusible body, but the quantity is insufficient to melt or render liquid the whole of the material, and coke is not formed.

"Investigators are in agreement that the true coking coals in addition

to the so-called resin-like bodies (which produce a slight coking effect) contain a class of substances which are not soluble in alkali, do not oxidize in warm air, and do not decompose or volatilize at 300° C, and that substances of this class melt when strongly heated, yielding enough luting or cementing material to form coke."

On p. 67 there is a good summary of the dye situation. "The outbreak of war demonstrated to the general public of the allied and neutral nations two cardinal facts which had long been appreciated by chemists having expert knowledge of the coal-tar industries. The first of these facts to attract public attention was the serious hindrance to great industrial undertakings in all civilized countries of the globe by the stoppage of German dyes. The interests affected in Great Britain alone were estimated at an annual value of £200,000,000 sterling. The second fact which became patent as the military exigencies involved an increasingly lavish use of artillery of all calibers was the intimate connection between the production of dyes and the manufacture of high explosives. In Germany the huge plants of the color factories were easily and swiftly diverted to the making of these essentials. The absence of such establishments in the allied countries was at first a serious drawback to any increased output of the required munitions of war.

"It was then seen that the existence of a well-organized coal-tar industry is one of the first essentials of national defense. Without an adequate supply of coal-tar products no nation can nowadays be self-contained and capable of maintaining its independence in arms without external help. Then arose the public outcry for the development and protection of 'key industries.' Outside the Germanic alliance each civilized nation, whether belligerent or neutral, strove to set its house in order as regards the production of synthetic dyes, this branch of manufacture being, on account of the above-mentioned facts, a key industry of fundamental importance. Reports of the action taken by the various nations have appeared from time to time in the public press and in the official publications of the respective Governments, and these notices are recorded in the pages of our Journal during the past two years.

"As all civilized countries are coal consumers, and some are also coal producers, it is evident that a determined bid will be made by each industrialized nation for the supply of its own synthetic dyes and other coal-tar derivatives. To this impending menace to their monopoly the German dye producers reply by opposing a united front, made up by combining their three existing syndicates in a huge trust, capitalized at more than £11,000,000 sterling. Assuming that other nations persist in their determination to develop their color industries, then it may be predicted with considerable certainty that the new epoch in the history of coal-tar dyes will find this industry in a condition similar to that of the brewing and distilling trades. In these industries the wants of each country in the way of alcoholic beverages are supplied by the brewers and distillers of the same nation. Only the choicest vintages and the most highly priced malt liquors find their way across the tariff walls of foreign consumers. It can scarcely be doubted that this will very soon be the condition of trade in the synthetic dye and drug industries. The local demand will be satisfied mainly by local producers, but certain very profitable specialties will command a world sale. In the competition of this foreign trade German manufacturers will for many years have tre-

mendous advantages arising from the possession of well-organized color factories, generously equipped research laboratories, comprehensive libraries, carefully compiled records, and an amenable personnel of thoroughly trained research chemists working under highly qualified direction in a scientific atmosphere. Added to these are the valuable material assets of cheap bromine, potash and other essential chemicals.

"It cannot in fairness be expected that other countries, which have hitherto neglected the factors which make for success in these highly technical industries, can hope immediately to divide the chief prizes with that nation which has assiduously developed each asset, whether material or personal, for more than forty years. Although considerable determination is being manifested on all sides, there is much leeway to make up.

"Another point which has recently attracted attention is the circumstance that the synthetic dye question is in reality part of a much larger problem, the conservation of our resources in fuel. Coal and other combustibles are frequently burnt in a shameful wasteful manner, no attempt being made to collect and utilize the escaping by-products. The economical combustion of our carbonaceous fuels, such as coal, lignite, peat, wood, etc., and the synthetic recovery of the by-products, ammonia, and tar, is the first essential step towards the establishment of a flourishing industry of synthetic dyes, drugs, and other fine chemical. Where fuel is wasted, tar products and their derivatives can never be manufactured cheaply and efficiently."

These extracts will give a fair idea of the general trend of the volume. They are not given as being the only interesting passages in the book.

Wilder D. Bancroft

A Text-Book of Sanitary and Applied Chemistry. *By E. H. S. Bailey. Fourth revised edition. 19 × 14 cm; pp. xxiv + 394. New York: The Macmillan Company, 1917. Price: $1.60.*—The book is divided into two parts. Under sanitary and applied chemistry the chapters are entitled: the atmosphere; fuels; heating and ventilation; lighting; water; purification of water supplies; sewage—disposal of household waste and garbage; textiles; cleaning—soap, bluing, and bleaching, disinfectants, antiseptics, and deodorants; poisons and their antidotes. Under chemistry of food the chapters are: food; cellulose, starch, dextrin, legumes; bread; breakfast foods and other special foods; sugars, glucose or grape-sugar group; leaves, stalks, roots, etc., used as food; composition and food value of fruits; edible fats and oils—food value of nuts; meat; eggs; milk, cheese, and butter; non-alcoholic beverages; alcoholic beverages; food accessories; preservation of food—coloring of food products; economy in the selection and preparation of food—dietaries.

There are a number of especially interesting minor points to be found in the book. On p. 218 the author says: "In the process of baking, bread will lose from 15 to 20 percent of its weight. This loss is due to the escape of carbon dioxide, gas, water, and alcohol. Elaborate attempts have been made to collect the alcohol that escapes during this process, but they have so far been failures. There is no small amount lost, however, as Liebig estimated that in Germany alone 12,000,000 gallons of alcohol disappeared yearly in this industry. There remains in the fresh bread, after baking, about 2 parts of alcohol

per 1000, and after a week this amount is diminished to 1 part per 1000. One author estimated that 40 2-lb. loaves contained as much alcohol as a bottle of port wine."

The paragraph on fresh and stale bread, p. 220, is also worthy the attention of the colloid chemist. "That there is a difference between fresh bread and that which is several days old is very apparent. What this difference is was for some time a question. It was formerly said that this difference was due solely to the loss of water, but that is proved not to be the case, as there is nearly as much water in bread after several days as when the bread is fresh, and if stale bread is reheated it becomes for the time fresh again. It has been suggested that in fresh bread some free water is present, which becomes united with the starch or gluten as the bread grows stale, and that reheating sets it free again. It has also been stated that the difference is only a 'molecular one.' Stale bread still contains about 45 percent of water. The true theory may be that as bread dries the fibers gradually approach nearer to each other by shrinkage, and the walls of the thousands of pores are consolidated, and the size of the pores is thus increased. When the stale bread is heated, expansion occurs; by the conversion of some of the water into vapor, the adhesion between the fibers is broken up, drawing them apart in the direction of the least resistance, producing an apparent diminution in the porosity."

On p. 235 we learn that "sugar was at first compounded with manna, and was supposed to be the dried juice of a plant. As it was not well understood, physicians regarded it as having an injurious effect upon the system. Honey was thought to be more wholesome, because a natural food." This has a very familiar sound. The use of ultramarines to counteract any yellow color in granulated sugar may be objectionable in making syrups because the fruit acids may set free hydrogen sulphide, p. 247.

The author is not enthusiastic about beef extracts, p. 287. "There has been much discussion as to the nutritive value of beef extracts, and the conclusion seems to be that the commercial extracts are not as valuable as a simple beef extract made by slightly broiling the beef and then squeezing out the juice. It is a mistake to suppose that 1 lb. of beef extract contains the soluble constituents of 20 to 30 lbs. of lean beef, and that, as Baron Liebig once taught, it is equal in nutritive value to this amount of beef. This extract lacks many of the most nutritious constituents, especially the proteins, and probably acts more as a stimulant and a substance to rouse the appetite for other foods, than as a true food. There are also preparations on the market which consist of extract of beef, to which some of the meat fiber has been added. (They are shown by analysis to contain some protein.) 'Beef juices,' which should be made by expression of the juice from the raw or slightly heated meat, contain considerable protein and are valuable nutrients.

"Referring to the fluid meat preparations, Thompson says: 'Usually they are tired of soon, and do not support life long, for, beyond the means employed of condensation of food by evaporation of water and compression, it is not possible to 'concentrate' nourishment very much. Making food assimilable and more useful is another matter from concentrating it in the sense that it can be made to support an able-bodied man and supply him with energy for a day's work, for example, of mountain climbing.'"

On p. 293 we read that "most of the so-called egg substitutes and custard powders consist chiefly of starch, dried skimmed milk, and turmeric or Victoria yellow; they are, of course, worthless as substitutes. * * * A convenient method for cooking eggs without the use of a thermometer, is to pour a quart of boiling water into a covered vessel, put two or three eggs into this, and allow them to remain five or six minutes. The yolk actually cooks more readily than the white, and by this process the eggs are cooked uniformly throughout."

The reviewer was glad to learn, p. 313, that "the difference between green and black tea is mainly due to the fact that the green is steamed thoroughly and then rolled and carefully fired, whereas black tea is first made up into heaps which are exposed to the air and allowed to ferment, and thus the olive-green is changed into the black color. * * * In England, black teas are used much more than the green. This is due to the fact that black teas contain less astringent matter and also act less upon the nerves. By comparison of analyses of black and green tea it is evident that there is less material soluble in hot water in the former."

There is an interesting summary on p. 368. "In general, vegetable food is cheaper than animal food, either as a source of energy or to build up the tissues. The reason for this is evident when we consider that the vegetable foods are built up from the simple substances found in air, water, and soil, while the food of animals consists of highly organized vegetable or animal substances. One author states, as an illustration of the comparative cost of vegetable food, that 2.5 acres devoted to raising mutton would support a man for a year, while the same amount devoted to the growing of wheat would support 16 men for the same time. It may be said that as the vegetable food is so much more bulky it would require much more heat to cook it; but, with the best appliances, the cost of this additional fuel would not counterbalance the increased cost of animal food.

"While carbohydrates are cheap constituents of food, proteins and fats are expensive. If the fat is derived from animal sources this is particularly true, but foods containing cottonseed oil, and the oil of some varieties of nuts, furnish fats at a reasonable price."   *Wilder D. Bancroft*

A Method for the Identification of Pure Organic Compounds. *By Samuel P. Mulliken. Vol. II. 26 × 18 cm; pp. ix + 327. New York: John Wiley and Sons, 1916. Price: $5.00.*—The second volume of this well-known series (volumes I and III have already appeared) includes the important compounds of Order II, or those containing the elements (*a*) carbon and nitrogen, (*b*) carbon, nitrogen and hydrogen, (*c*) carbon, nitrogen and oxygen, (*d*) carbon, nitrogen, hydrogen and oxygen. Essentially the same plan has been followed in this volume as in the preceding volumes of the series, though certain details have been modified in such wise as to afford distinct improvement. The fourth and concluding volume is promised in the not distant future.   *T. R. Briggs*

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